Air-drying and osmotic dehydration of banana: their effects on changes of volatile components of dehydrated product

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AIR-DRYING AND OSMOTIC DEHYDRATION OF BANANA: THEIR EFFECTS ON CHANGES OF VOLATILE COMPONENTS OF DEHYDRATED PRODUCT.

A thesis submitted in (partial) fulfilment of the requirements for the award of the degree of

MASTER OF SCIENCE
With Honours
from

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by

THI MINH HUE NGUYEN, BSc

Supervisor - A. Prof. William. E. Price

Department of Chemistry

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ABSTRACT

The effect of air-drying and osmotic dehydration of banana slices (Cavendish variety of Australia) on the flavour and volatile components of dried banana was studied. This was conducted to obtain a better understanding of the drying kinetics of banana, and the influence of process parameters on maintaining or enhancing the quality of dried product in terms of volatile retention.

Air-drying of banana was found to occur mainly in the falling rate period. A diffusion model based on Fick's Second Law was used to predict the changes of moisture content as a function of drying time at different temperatures, and thickness of banana slabs. Green and ripe banana slices were dried to investigate the influence of different maturity of banana on the drying behavior.

The effects of process parameters (temperature, concentration, and sugar nature) on the kinetics of moisture loss and solute uptake in osmotic dehydration of banana slabs were also studied. The results indicated that the effect of temperature was more significant than syrup concentration on both water loss and solute uptake in the process. The different solute uptake between green and ripe banana was found to be related to the difference in tissue structure and carbohydrate contents between these bananas. Banana slabs, which had undergone osmosis and then air-dried were more
appealing in color and texture compared to the air-dried banana. As the sugar content of osmosed banana increased through the osmotic treatment, the drying rate during the subsequent air-drying of the banana fell, and it could be seen that the level of solute uptake played the key role in reducing the drying rate.

Headspace Solid Phase Micro-extraction (HS-SPME) in conjunction with gas-chromatography-mass spectrometry (GC-MS) used to extract and identify the volatile profiles of fresh, air-dried and osmotically air-dried banana. The optimal conditions for HS-SPME of banana volatiles were determined. The loss of banana volatiles was found to be strongly influenced by the dehydration conditions especially the initial drying rate. The effect of osmotic dehydration prior to air-drying on the retention of banana volatiles was investigated. The optimal osmotic conditions were found to be osmotic dehydration at 30°C using 60% sucrose solution for six hours. The multi-step drying approach with an initial short period of high temperature air-drying followed by osmotic dehydration and subsequent lower temperature air-drying gave the best retention for volatiles in the dried product.
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CHAPTER ONE

INTRODUCTION
1.1. THE FRUIT.

1.1.1. History

Most authors agree that banana originated in the Indo-Malaysian region of southeastern Asia. [1-3]. From there, they spread into Hawaii, South America, Africa, Latin America and elsewhere. The banana industry in Australia is well over 100 years old [4] with the first commercial plantings started in 1883 in Queensland [4].

1.1.2 Varieties of Banana.

Bananas belong to the family Musaceae and consist of 2 genus: Ensete and Musa. There are 200-500 varieties of bananas and plantains [5]. Bananas (Musa acuminata) are generally eaten raw, whilst plantain (Musa paradisiaca) are cooked [1]. Figure 1.1 shows the range schematic of banana varieties.

From this figure, except for the Fe’i, all the edible bananas belong the Eumusa section of the genus Musa. Eumusa section has of two wild species: M. acuminata (A), and M. balbisiana (B). Although there are numerous cultivated varieties, the two principal one are Cavendish and Gros Michel [1]. There is little difference between these two, but Cavendish has a lower susceptibility to disease, a higher ability to withstand strong wind, and gives higher yields than Gros Michel does. Ripe Cavendish banana is greenish, fruit tips are blunt, and the fruit is markedly curved [1].
Gros Michel bananas give large fruit, which are bottlenecked, and bright-yellow when ripe. This variety is very susceptible to Panama disease, which causes the
complete destruction of the tree by wilt. Therefore, throughout the world bananas for export come entirely from the Cavendish variety.

In Australia, Cavendish and LadyFinger are two the main varieties of banana [4]. LadyFinger bananas of Australia belong to AAB subgroup (Figure 1.1). LadyFinger bananas are sweeter, smaller, and more acid in flavour than Cavendish. The fruit of this variety has a very thin skin, is bright yellow when ripe and does not turn brown when cut [1]. However, it represents less than 5% of Australian production.

1.1.3 Fruit morphology and anatomy.

The banana plant is large and tree-like (Figure 1.2). It grows to a height of 3-9 meters. [1-3]. A pseudostem consists of leaf sheaths and large leaves. The flower stem bears bunches of small tubular flowers [1], which develop into clusters (hands) of fruit [5]. It takes from two to six months for a hand to reach maturity. It consists of individual fruit called fingers. Distal flower clusters are male and do not produce fruits. Fruit develops from the inferior ovary of the female flower [5]. It develops without the stimulus of pollination. The ovules shrivel early and can be seen in the central part of the fruit as brown flecks. Most of the pulp is developed from the inner face of the skin [2]. Green banana contains a large amount of starch. During ripening, the starch is progressively depleted within pulp cells. The peel (skin) tissue makes up 80 %, 40 %, and 33 % of the weight of very green, ripening and fully ripe banana respectively [7]. As the banana ripens, water moves from the peel to the
pulp due to increased osmotic pressure in the pulp, which is caused by the hydrolysis of starch.

Figure 1.2: The banana plant [5]
1.1.4 The production and trade of banana and its products.

Banana is a major product in Australia's fruit industry [8]. Bananas are grown mainly on the coastal plain in the tropical north and southeastern Queensland (Queensland production accounts for 80% of Australia's crop [8]). The second largest production area is the North Coast of New South Wales (Coffs Harbour) [9]. Bananas are also grown in Carnarvon (and to a lesser extent in Kununurra) in Western Australia. In the Northern Territory, bananas are grown near Darwin [10].

The two main varieties of bananas in Australia are Giant Cavendish (major) and Lady Finger. The main types of Cavendish variety are Williams Hybrid (in New South Wales) and Grain Nain in Queensland (often called Mon Mari). The main type of Lady Finger is Goldfinger [11]. This type is of some importance in trade and local consumption in Eastern Australia [2].

Worldwide, banana represents the most important fruit crop in terms of both production and trade [1, 5, 9], and it is the fourth largest rural product (in dollars terms) behind rice, wheat and milk [3]. Cavendish is the most common variety produced in the world [5]. Latin America (Brazil, Ecuador) produces the world's largest banana crops. Other major producing countries are Hawaii, Philippines and China [12]. Transportation of ripening bananas to the markets is still the main problem in the exporting of raw banana, due to slight blemishes, over-ripeness, or
mechanical damage. As a result of these phenomena, dried products are becoming increasingly more popular.

Ecuador has been the major supplier of dried banana to European markets [13]. France, Germany, and the United Kingdom are the largest importers of dried banana products [13]. Dried banana is also becoming more common on the US market, as a low fat snack food.

1.1.5 Nutrition and chemical compositions of banana.

Bananas are a very nutritious, healthy food because they contain less than 2% fat [10, 14], contain no cholesterol, and are very low in sodium (this is of benefit for people with high blood pressure). In addition, they are a good source of fibre (one banana can supply 16% of daily need of fiber [15]), carbohydrates, vitamins A, C, folate, B₃, B₁ and B₆ [5, 8, 10, 12, 14, 16, 17]. Banana is especially very rich in potassium, helpful in the prevention of heart disease and maintaining healthy cardiovascular muscle. Due to the abundance of potassium and B₆ in banana, the fruit is considered as a nutrient for the brain [10] (since potassium is needed for proper brain function). Moreover, with a high level of B₂, banana helps the body break down carbohydrates and fat, and is therefore beneficial for weight control.

Ripe banana has a very high sugar content [17] in comparison to that of other fruits.
Cavendish banana has the highest level of sucrose (8-10 g/100 g) among fruits with high sucrose levels such as rambutan, mango, and jackfruit. Percentages of glucose and fructose in banana are very similar (both in green and ripe banana). There are significant differences in sugar content between green and ripe banana as well as between raw and dried banana. Other sugars found in banana are maltose, mannose, galactose, rhaminose, raffinose and melezinose [18]. The amount of sugar in green and ripe banana as well as in dried banana shown in Table 1.1.

Table 1.1: Sugar content in raw and dried banana

<table>
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<tr>
<th></th>
<th>Sucrose</th>
<th>Glucose</th>
<th>Fructose</th>
<th>Total</th>
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<td>Green banana,</td>
<td>0.5 - 2.2</td>
<td>0.2</td>
<td>0.05 - 0.5</td>
<td>0.8 -1.3</td>
<td>19-21</td>
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<tr>
<td>(% fresh pulp)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ripe banana</td>
<td>8.8 -10</td>
<td>2.5 - 4.2</td>
<td>2 -5</td>
<td>14 - 25</td>
<td>1, 5, 16, 17, 19-22</td>
</tr>
<tr>
<td>(% fresh pulp)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dried banana</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>88.6</td>
<td>1, 16, 22</td>
</tr>
<tr>
<td>(% dry matter)</td>
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Starch accounts for more than 20% w/w of green banana pulp [19-22]. The amount of starch drops markedly (to 1-2%) in fully ripe banana. This depletion of starch results in the softening of fruit during ripening through the changes in physical characteristics of banana tissue such as decreased elasticity, viscosity, and firmness [21, 23, 24]. This is caused by the collapse of cell walls, and the loose arrangement of cells [25].
Changes in carbohydrate content (both starch and sugars) during ripening of banana have been found to be influenced by the temperature used to ripen and store bananas. In general, the higher the temperature used, the higher the sugar content (and hence lower amount of starch) found in ripe banana. Maximum sugar content were found in banana ripened at 25°C [2, 24]. However, bananas ripened at this temperature are susceptible to mechanical injury and exhibit a reduced shelf life [24].

1.1.6 Volatile Constituents of Banana

The composition of volatile flavours of fresh banana has been studied previously. At least 350 compounds were separated by Tressl et al [26], of which 180 constituents were identified. Banana volatile compounds consisted mainly of acetate and butyrate esters, which give the fruit its distinctive aroma and flavour. Alcohols are the second class of major volatile constituents of fresh banana, with butyl and amyl alcohols predominating. Besides these compounds, aromatics such as eugenol, elemicin and methyleugenol are typical volatile constituents of fresh banana [26].

Maturity has been reported to influence the qualitative and quantitative compositions of banana volatiles. Previous studies showed that the volatile compounds of banana only formed in ripe fruit. Intensive studies on the changes and biogenesis of volatiles during the ripening of banana have been reported by many
authors [27-32], and precursors of these compounds have also been determined [22, 28, 33-38]. Major esters and alcohols are formed from the degradation of amino acids such as leucine, valine, isoleucine during ripening of banana, or from the metabolism of fatty acid in banana [28].

Changes of volatiles during banana drying have rarely been reported in the literature. Only the report of Uzelac [39] was considered relevant to this matter. Extraction and identification of volatiles compounds were done using conventional extraction techniques such as solvent extraction, vacuum distillation and headspace analysis using GC or GC- MS. Recently, Picque et al [40] used solid phase microextraction technique for direct extraction of freeze drying banana volatiles. Cryogenic headspace extraction and direct solvent extraction were applied to extract volatile of dried banana (SalePiasang products, Indonesia) [41].

1.2. COMMERCIAL BANANA PRODUCTS.

1.2.1. Different commercial products of Banana

In general, bananas are eaten raw in the ripe state. Only a small proportion is processed to obtain a storable product. Although preserved products do not contribute significantly to the global diet, in some local areas, however, these products are important in periods when bananas are scarce.

Preserved banana are found in the following forms:
- Banana puree made from mashed ripe pulp. This product is canned and used as an ingredient in dairy desserts, drinks and bakery food [1, 5]. This product can remain stable for at least 6 months [1].

- Canned banana slices or chunks in acidified syrup are used in fruit salads, desserts, drinks and bakery items [5].

- Banana flour is prepared from unripe banana and plantains by sun drying of banana slices [1]. Essence extracted from ripe pulp is normally added to the flour [5].

- Banana flakes, which are prepared by drum drying, or freeze drying slices, are other less important products. These products are used in breakfast cereals.

- Banana chips are produced as a snackfood from thin unripe banana slices. Firstly, a chemical treatment (usually sodium metabisulphite is used) is applied to keep the product white. The banana slices are deep fried in hydrogenated oil at 180-200°C [42]. Various flavourings and antioxidant are added to the final product (for example, coconut). Other products are dried - bananas. They are produced using a traditional processing or industrial processing. The product was found stable to microbial spoilage when bananas were dried to 14-15 % wet basis at 60°C (aw = 0.55) [5].

- “Figs” are whole or halved ripe bananas, which are produced by means of sun drying. They have an unattractive color–dark brown, but pleasant flavor. Due to high content of sugar in ripe banana, this product can be kept stable for a long time (surprisingly, it is said to store satisfactorily for over 10 years [5]).
1.2.2 Industrial processing of dried banana.

To obtain a good quality of dried product, banana are harvested at the appropriate maturity and ripened under controlled conditions [42]. They are picked in the green state, and ripened at a temperature of 14-21°C [43] for 4 –7 days [35] with a high relative humidity (at least 80 % [43]). Ripening is initiated with 1000 ppm of ethylene. If banana is stored under 14°C, it will suffer chilling injury, which can be detected by a browning of the peel. This makes the pulp lack flavour, sweetness, and such fruit tends to be acidic astringent, and unable to ripen normally.

Fully ripe bananas (with sugar content of 19.5 % or above) are used to produce figs. After peeling, bananas are treated with sulphurous acid (usually for 20 min), then immediately dried by means of air-drying. Temperatures used are in the range of 50°C to 82°C with drying times of 10 h [42] to 72 h [12] down to moisture contents from 8 % to 18 % [42]. Harney and Co produces most of the dried banana made in Australia, from fruit grown at Coffs Habour [44]. In one Australian factory, solar heat collectors are used to augment the heat for drying banana [42]. Tunnel and cabinet dryers are often used. Buckle et al [44] describes the dehydration of banana using solar drier cabinets, the process taking 72 hours, at 50°C to reach a 15 % moisture content.

To improve the product quality, a combined “osmovac” process has been applied for sliced banana [4, 42]. Vacuum drying is usually carried out at 66 –71°C,
10 mm Hg. Sulphiting the fruit before drying to inactivate the oxidases has been proposed for prevention of discoloration. (1 min, in 2000 ppm sulfur dioxide)[42].

1.3 PREVIOUS WORK ON DEHYDRATION OF BANANA.

Most previous work on drying banana has focused on atmospheric drying. Air-drying was the most common method applied in previous studies. In this method, both heat transfer and mass transfer simultaneously occur. Heat from the hot air is transferred to the fruit and its energy activates the moisture movement. The removal of water in foodstuff during drying occurs via two mechanisms: migration of water within foodstuff and evaporation of moisture from foodstuff into the air. The former is considered as the most common moisture migration during drying, and has been used to explain the drying kinetics of banana [45-47].

Modelling of the drying kinetics of banana has been carried out by some authors. Mowlah et al [46] applied Fick's law of diffusion to predict drying behavior of banana. The predicted drying time fitted well with experimental data [46]. A one-parameter empirical mass transfer model for drying banana was proposed by Kiranoudis et al [48]. In this model, drying constant was used as a function of processed variables (temperature, dimension of samples, humidity). This model was applied to the drying of four fruits namely, apple, pear, kiwi fruit, and banana. Wang et al [49] gave a diffusion model, in which the effect of heat transfer besides mass transfer were taken into account. Their results showed that the most intensive heat and mass transfer occur in the transition region, where capillary flow and
vapour diffusion play an important role. A variable diffusion model was proposed by Garcia et al [47]. In this work, banana slices and foam were dried using microwave and air ovens. The report showed that mass transfer by vapour diffusion mechanism was intensified in microwave drying.

The effects of drying conditions and drying methods on quality of product were reported. Krokida and Maroulis [50] examined the effect of microwave and microwave-vacuum on increased product porosity and decreased color damages. They showed that microwave drying increases elasticity and decreases viscosity of product [50]. Krokida et al [51] studied the effect of freeze-drying conditions on shrinkage and porosity of banana, potato, carrot, and apple. They found that final porosity decreases as sample temperature increases. These authors [52] also examined the effect of drying conditions on color change during conventional and vacuum drying those fruits. Rate of color changes was found to increase as temperature increased and air humidity decreased. Robinson [53] investigated the improvement for banana dehydration and designed the dried banana plant at Coff's Harbour, Australia.

Osmotic dehydration of banana has been of the interest to many authors [45, 54-58]. It is not only a dehydration method, but also the means to improve the quality of dried fruit. There are many factors, which influence the rate of dehydration, as well as the ability of osmotic dehydration to maintain good sensory qualities for the dried products such as flavour, and colour. Therefore, previous work has focussed on developing a suitable model to predict osmotic dehydration kinetics. Two kinds
of models for this process have been proposed. The first model was a diffusion model, where the mass transfer during osmotic dehydration of banana was assumed to follow normal Fickian diffusion. This model was reported by Rastogi et al [56], Mauro et al [55] for cylindrical pieces of osmosed banana, and Waliszewski et al [59] for osmotic dehydration of banana chip. Due to the complexity of the osmotic process (i.e. the mass transfer is strongly influenced by a range of experimental parameters) some authors have proposed alternative empirical models [54, 57, 60, 61].

Adambounou and Castaigne [58] presented isotherm sorption curves of osmosed banana following by vacuum drying. To date, only one report of Sankat et al [45] on the air drying behaviour of osmotically dehydrated banana has been published. Recently, Garcia et al [62] examined twenty-seven conditions of osmotic dehydration for monitoring color changes in banana during processing. These conditions included variations in temperature, sugar concentration, and pH of osmotic agents.

1.4 AIMS OF PROJECT

The major aim of this work is to determine optimum drying conditions for dehydration of banana in terms of maintaining of the “fresh-like” quality and flavor of the dried product. In order to attain this goal, the work is divided into the following topics:
1. **Investigation of the major factors which influence moisture transport in air-drying of banana.** Experimental parameters of drying temperature, size of samples and other factors will be investigated. In addition, the effect of fruit maturity on the drying kinetics will be examined. This latter factor has not been reported previously.

2. **Optimal conditions for osmotic dehydration of banana.**

Two major studies will be carried out. The first investigation is the effect of osmotic parameters such as temperature, sugar concentration, and kinds of sugar on the rate of osmotic dehydration. Although this has been looked at previously by some authors, in this work, the rate of osmotic dehydration is not the sole aim. The major aim is to find the relationship between the different osmotic conditions, and the influences of osmotic dehydration on subsequent air-drying of osmosed banana. A better understanding of this relationship will be useful in applying osmotic dehydration effectively as a pretreatment to air-drying, as a way to minimise loss of banana volatile flavours during drying. The second investigation is to find the role of different microstructures of fruit at different ripening states on the mass transfer process. This has received little attention previously.

3. **Identification and monitoring of changes of volatile constituents of banana during drying using SPME technique.** This work was divided into three parts:

   Optimizing sampling conditions for applying SPME technique to extract volatile constituents of banana.

   Investigation the effect of drying conditions (temperature and thickness of sample) on the loss of these compounds.
Evaluation the effect of osmotic dehydration on reducing the loss of volatile banana during drying, and optimizing osmotic parameters to maximize its effect on maintaining volatile constituents of banana.
CHAPTER TWO

AIR-DRYING OF BANANA
2.1 INTRODUCTION

All food contains water. Food with high water content has been observed to have a high rate of deterioration. This is usually expressed in terms of the food’s water activity ($a_w$). Water activity is the ratio of water vapor pressure over a food ($p$) to that over pure water ($p_0$) [63]. Water activity $a_w$ is the most commonly used criterion for safety and quality of food in terms of stability for storage. Dehydration to lower $a_w$ is the most common and oldest way for the preservation of fruit.

Drying is the process of removal of water from food, usually using heat. This process consists of heat and mass transfer. Water movement is caused from internal moisture movement (the migrations of water in the food matrix) and the external moisture movement (the evaporation from the surface) as illustrated below [64].
Which of these processes will govern the rate of drying depends on the state of water in the food (free or bound water), the drying conditions (temperature, humidity, velocity of air etc...) and any microstructural changes in the food due to different maturity or changes during the drying process. Generally, drying in foods is characterised by two separate phases: the constant rate and the falling rate periods.

For a high-moisture food, prior to drying, the surface of the food is saturated with water [65]. When water from the surface evaporates, this water is replaced by water, which transfers from the interior to the surface and maintains the surface in a saturated state. The difference between the vapor pressure of water at the food surface and the partial pressure of water in the air is the driving force [66]. The drying rate is thus constant for a period of time until the migration of moisture to the surface is not sufficient to keep it in a saturated state, assuming the composition of the drying air does not change. The constant rate period ends and the moisture content at this point is referred to as the critical moisture content. The falling rate period then starts, and the drying rate falls monotonically to the end of process. Fruit with a high amount of free water (i.e. unbound water in food sites due to no chemical bond, or ion-dipole force) and fruit with a skin such as plum, grape, apple, apricot, peach, and pear usually undergo a constant rate period during drying process if the drying temperature is not too high.

The drying rate during the falling rate period is caused by the concentration gradient of moisture inside the food matrix. The internal moisture movement results from a number of mechanisms such as liquid diffusion, capillary flow, flows due to
shrinkage and pressure gradients [67]. A capillary mechanism usually occurs in porous material. Inside this material, there are various capillaries of different radii. These are interconnected and whenever a difference of capillary pressure occurs, moisture from large capillaries will transport to small ones by capillary suction [68]. It is then carried to the surface.

Liquid diffusion is the most common mechanism, which describes and predicts well the drying kinetics of many foods in the falling rate period. Fick’s law of diffusion can describe the principle of this mechanism according to the following equation:

\[
J = -D \frac{dc}{dx}
\]

Where \( J \) is rate of molecular diffusion mol/(m²s) [67].
\( D \) is the diffusion coefficient (m²/s).
\( \frac{dc}{dx} \) is concentration gradient (mol/m³).

Some foods experience an immediate falling rate period at the beginning of drying. For example fish [69], corn grain [70], sugar beet root [71], potato [72], kiwi fruit [48]. The amount of free water in these foods is low, and therefore after free water evaporates (for short time), drying rate falls due to bound water inside food needing time to migrate to the surface. In addition, only water close to the surface is easy to remove, whereas water in the deeper sites of the food takes a longer time to diffuse to the surface.
Moreover, the drying rate during this stage depends on the properties and microstructure of the food tissue. The removal of water from the food during this period becomes more difficult as drying proceeds. This may be due to the collapse of cells which hinders the pathway, the contract of free space due to shrinkage, increased viscosity and sugar concentration as solid content rises, and case hardening due to drying at high temperatures of all which cause a surface barrier to moisture movement.

Two falling rate periods are observed for some dried food such as fish, corn grain, potatoes, apple, skim milk, coffee extract and banana [45, 69, 70, 73, 74]. The second falling period occurs at low moisture content. The presence of a second falling rate period could indicate changes in water diffusion coefficient. This is understandable as diffusivity is concentration dependent, therefore at low concentration, drying follows another drying period of lower water diffusivity than that of in the first period. Another explanation for the presence of two falling rate periods is that the surface of food is dry after the first falling rate. In this case, the plane of evaporation moves down into the wet solid (moving boundary), where the vapour must travel through the dried layer. This makes the movement more difficult, and as a result, the rate is reduced.

Due to the complexity of food, drying can occur simultaneously by different mechanisms. Therefore, modelling the drying process, and predicting the drying behavior under different conditions is necessary to have a better understanding of the mechanisms of drying at play. Fick's law of diffusion has been used to describe the drying kinetics of fruit during the falling rate period.
Modelling the drying of banana has been reported by Garcia [47], Sankat et al [45] and Molah [46] using Fick’s law of diffusion.

Although there have been some studies [46-48] on dehydration of banana, these have focussed on the validation of a particular model, under a limited range of drying conditions. The effect of temperature on the drying kinetics was of most interest in these studies. In addition, there were some inconsistencies in the derived diffusion coefficients, (D = 8.33 x 10^{-10} m^2/s [46], and 34.8 x 10^{-10} m^2/s [45], at 60°C, 1 cm slabs). It was therefore of interest to reinvestigate the matter as a preliminary exercise to studying osmotic dehydration, and the changes in volatile composition during drying. This is worthwhile in order to have a better understand of drying behavior. This in turn can help to obtain good quality control for the dried product.

The aim of this current work is to investigate the effect of drying conditions on the drying kinetics. Focus was put on different drying air temperatures over a wide range from 30°C to 70°C, and the thickness of slabs. The influences of banana nature (i.e. maturity, and variety of fruit due to different harvesting seasons) were also studied to confirm the effect of morphology on the drying kinetics. This is useful, because significant changes in structure, as well as changes of chemical compositions occur during ripening of banana, which can affect the drying behavior of banana of different maturities.
The influence of drying conditions on mass loss (both water and of others such as volatile compounds) is also important to the later examination of changes of volatiles in air-drying and osmotic-air drying of banana in other sections of this work.

2.2 EXPERIMENTAL METHOD

2.2.1 Materials:

Fresh bananas of Cavendish variety were used in this study. Bananas were bought from commercial sources in Wollongong, Australia. They were grown in North Queensland, Australia. Ripe bananas (bright yellow) and green bananas were used in drying studies. Experiments were repeated in different months from January to November to obtain reliable results, and to examine the effect of various harvesting seasons on drying kinetics. In order to ensure that there is not much change in maturity of fruit, bananas those were subjected to drying were not left more than 4 days after purchase. They were stored at room temperatures, from 18 °C to 24 °C depending on different seasons around the year.

2.2.2 Drying Procedures

Bananas were peeled and weighed using an analytical balance with a sensitivity of ±0.001g. After weighing, bananas were cut into cylindrical pieces of thickness 1 cm or
2 cm. Three hundred grams of ripe bananas, without any treatment, were used in each experiment.

Drying experiments were carried out using a laboratory-scale system. This system was designed by Sabarez [75]. It consists of a dehydration unit and an online datalogging data system. The drying chamber was equipped with heating, ventilation, and a humidifying system [75]. The humidifying system was used to control the humidity during drying. The fluctuation in RH% that occurred during the experiments was better than ± 5%. Fruit was placed on a stainless steel mesh tray, which was suspended from an electronic balance. The balance output to a computer-based data acquisition system recorded automatically the mass change, temperature, and humidity of surrounding air as a function of drying time. This system is illustrated in Figure 2.1.

Drying experiments were carried out at 10°C intervals between 30°C and 70°C. The air velocity was set at a constant 1 m/s. All experiments were repeated at least three times. All drying experiments were continued until a constant mass was obtained (i.e. constant values were recorded in the computer for at least four hours).
2.2.3 Moisture Content Determination.

Initial moisture contents of banana were determined by vacuum drying at 60°C, for 48 hours [54] over magnesium sulfate desiccant. The initial moisture contents were determined for bananas grown at different times throughout the year. The average value was used to interpret data. The initial moisture contents were expressed on a kg/kg dry basis.
2.3 RESULTS and DISCUSSION

2.3.1 Moisture Content of Banana

The average initial moisture content of Australian fresh banana during experiments from March to November was 74.7±1.3 % on wet basis or 2.96 kg/kgDM. This value agreed well with reports from the literature [5, 17, 76-78]. Higher moisture content for banana harvested in January was 77.8 ±1.4 % on wet basis or 3.5 kg/kg DM. This value also agreed with results from other authors [25, 45-46, 80].

Commercially, banana was dried down to less than 20 % final moisture content [44, 53, 81], or usually dried down to 14-15 % final moisture content (on dry basis) [12, 16, 47]. This corresponded to 69.7% mass loss (20% final moisture content) or to 71.2 % mass loss (14 % final moisture content) in this work. At such a level of moisture content, dried banana has a shelf life at least 6 months [53].

In this study, low humidity was used for drying at 50°C, 60°C, 70°C, and higher humidity was applied for cases of 40°C, 30°C. Low humidity was applied to obtain a higher rate of mass loss. Humidity during drying was reproducible for different runs of banana from different months and it did not vary significantly during a run. In most cases the standard deviations of three replications were not over 3 % (Except at 30 °C), as shown in Table 2.1.
Table 2.1: Relative humidity ranges of experimental drying of banana at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average of RH%</td>
<td>45.8</td>
<td>27.4</td>
<td>8.9</td>
<td>5.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>8.3</td>
<td>2.3</td>
<td>0.6</td>
<td>1.4</td>
<td>0.7</td>
</tr>
</tbody>
</table>

2.3.2 Modelling the Kinetics of Air-Drying of Banana

2.3.2.1 Theoretical Models

In order to describe the drying behavior of banana, and predict it under different drying conditions, it is necessary to model the drying process. As known from the literature, drying of banana mainly follows a falling rate profile. Mass transfer during this period is caused by liquid diffusion or capillary flow. The former is commonly used to describe drying behavior in the falling rate period of fruit and vegetables. The rate of diffusion is governed by moisture concentration gradient as the driving force. Fick’s law of diffusion is widely used to model the drying behavior for this period [82].

Fick’s second law of diffusion can be expressed as:

\[
\frac{dW}{dt} = D \frac{d^2W}{dL^2}
\]  \hspace{1cm} (2.1)
Where \( W \) = moisture content at time \( t \)

\[ L = \text{distance (m) in the direction of diffusion} \ [67] \text{ (or thickness)} \]

\( D \) = liquid diffusivity. \( (m^2h^{-1}) \)

If the external mass transfer resistance is negligible, mass transport occurs in one dimension, and initial moisture content is assumed to be uniform in slabs. A well-known analytical solution for (2.1) was given by Crank [83] for an infinite slab drying from one face [84]:

\[
\frac{(W-W_t)}{(W_0-We)} = \frac{8/\Pi^2 \left[ \exp \left\{-Dt (\Pi^2/4L^2) \right\} + 1/9 \exp \left\{-9Dt(\Pi^2 (W_0-We)/4L^2) \right\} + \ldots \right\}}{(W_0-We)} \]

(2.2)

For long drying time [84-85], (2.2) can be reduced to:

\[
W_r = \frac{(W - We)}{(W_0 - We)} = \frac{8/\Pi^2 \left[ \exp \left\{-D. t (\Pi^2/4L^2) \right\} \right]}{(W_0 - We)} \]

(2.3)

Where,

\( W_e \) = Equilibrium moisture content (dry basis)

\( W_0 \) = Initial moisture content (dry basis)

If moisture loss occurs from both sides, \( L = \) half of thickness of slab.

Both equations 2.2 and 2.3 ignored the initial thermal transient.

Equation (2.3) can be rewritten as:

\[
W_r = A e^{-Kt} \]

(2.4)
Where $K$ is a drying constant $(h^{-1})$, $Wr$ is removable moisture ratio, $t$ is drying time (h), and $A$ is a constant.

The values of $K$, and $D$ may be obtained from the slope of the plot $\ln (Wr)$ versus drying time according to equation (2.3) and (2.4) respectively. This plot should be a straight line. To apply the equation (2.3), the most important quantity is the equilibrium moisture content. A number of empirical equations exist in the literature for calculation of equilibrium moisture content in banana as following:

1. **Henderson’s equation [47]:**
   
   $$W_e = - \left[ \ln \left( \frac{1-Rh}{k (T+c)} \right) \right]^{1/n}$$

   Where $n$, $c$, $k$ are empirical constants, and $T =$ temperature (K)

2. **Henderson’s equation [86]**
   
   $$1 - a_w = \exp (-k W_e^n)$$

   Where $k$ and $n$ are constants at a particular temperature.

3. **Iglesias and Chrife [86]**
   
   $$W_e = k \left[ a_w / (1 - a_w) \right] + c$$

   Where $k$ and $c$ are constants at a particular temperature.

4. **The Guggenheim, Anderson and de Boer (GAB) equation [48].** This equation was used to calculate the $We$ using sorption isotherm data measured at static equilibrium states.
   
   $$We = k a_w / (1 - b a_w) (1 + c a_w)$$

   Where $k$, $b$ and $c$ are constants at a particular temperature.
However, in the present work, wide variations in calculated equilibrium moisture content were obtained from these equations under the conditions used here. This is mainly because the range of conditions under which the equations were derived differed from the conditions employed in the present study. Moreover, the differences might be due to varietal differences of bananas. The examples are summarized as follows:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Equation</th>
<th>RH % of experiments</th>
<th>We (kg/kgDM) (of experiments)</th>
<th>We from literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>(1)</td>
<td>46%</td>
<td>0.116</td>
<td>0.10 ( RH =50%) [86]</td>
</tr>
<tr>
<td></td>
<td>(4)</td>
<td></td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2) or (3)</td>
<td></td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.247 ( at the end of drying)</td>
<td>0.25 (RH= 45.8 %) from data of sorption isotherm [48]</td>
</tr>
<tr>
<td>50°C</td>
<td>(1)</td>
<td>8 %</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(4)</td>
<td>8 %</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

From this table it could be seen that even at one drying condition (temperature) large variations of We obtained using these different equations.

Most data of sorption isotherms reported for banana were done at low temperatures (e.g. 25°C [48, 86-88], 35°C, and 45°C [86]). These temperatures however, are not practical in industrial drying, and drying at higher temperatures (60°C, 70°C) was mainly carried out in this work. Consequently, equilibrium moisture contents at these
high temperatures could not be calculated from literature sorption data. [48, 86, 87, 89, 90]. Therefore, an empirical method for estimating equilibrium moisture content was proposed in this study. In this method, equilibrium was obtained when drying rate is zero, i.e. when $dW/ dt = 0$. The values of equilibrium moisture contents were determined by the point on the plots of $dW/ dt$ versus $W$ when the graph cuts the moisture axis. This approach can be applied as the drying occurred over a long time, when equilibrium could be approached. This method was the best available within the time constraints of the project. More time-consuming isotherm measurements were outside the scope of the work. It was interesting to see that the results obtained in this study were very similar to results reported by Sankat et al [45] using the same method and with the same range of RH% at each drying condition.

2.3.2.2 Results and discussion for estimated parameters of diffusion model.

The equilibrium moisture contents for all drying conditions obtained in this study are summarized in Table 2. 2. The results of equilibrium moisture contents agreed well with data in the literature.

Applying equation (2.3), by plotting the natural logarithm of removal moisture ratio ($W_r$) versus time, the value of rate constant ($K$), and thus the diffusion coefficient $D$ could be determined from the slope of the straight line.

\[ \text{Slope} = - \frac{\pi^2 D}{4L^2} = K \]  

(2.5)
Where \( L \) = the thickness of the slab, if drying occurred only on one large face. In this study, drying occurred on two faces, as slabs were placed on a mesh tray. In this case \( L = \) half thickness.

Table 2.2: Equilibrium moisture contents of banana at different drying conditions.

<table>
<thead>
<tr>
<th>Drying conditions</th>
<th>Values of ( W_e ) (kg/kgDM)</th>
<th>( W_e ) in the literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 °C, 1 cm</td>
<td>0.25</td>
<td>0.27 [48]</td>
</tr>
<tr>
<td>40 °C, 1 cm</td>
<td>0.22</td>
<td>0.23 [45]</td>
</tr>
<tr>
<td>50 °C, 1 cm, green</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>50 °C, 1 cm, ripe</td>
<td>0.16</td>
<td>0.16 [45], 0.2 [calculated from GAB of [48]]</td>
</tr>
<tr>
<td>50 °C, 2 cm, ripe</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>60 °C, 1 cm, green</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>60 °C, 1 cm, ripe</td>
<td>0.095</td>
<td>0.11[45]</td>
</tr>
<tr>
<td>60 °C, 2 cm, green</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>60 °C, 2 cm, ripe</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>70 °C, 1 cm, green</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>70 °C, 1 cm, ripe</td>
<td>0.09</td>
<td>0.13 [45]; 0.08 calculated from GAB of [48]</td>
</tr>
<tr>
<td>70 °C, 2 cm, green</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>70 °C, 2 cm, ripe</td>
<td>0.13</td>
<td></td>
</tr>
</tbody>
</table>

Note: In all cases, the standard deviations in the mean \( W_e \) were between 1-3% for three replications.
Figure 2.2 shows the plots of \( \ln \text{Wr} \) versus time for banana (1cm) dried at different temperatures.

**Figure 2.2:**

Plots of \( \ln \text{Wr} \) versus time for 1cm slabs banana versus time at different drying temperatures. (Initial moisture content = 72.6 % wet basis, velocity =1m/s)

From Figure 2.2, the linear plots of \( \ln \text{Wr} \) versus time indicated that \( D \) was independent of moisture content. \((R^2 = 0.99 \text{ for all temperatures.})\). Increased \( D \) with increased temperature was observed. Values of constant rates and diffusion coefficients obtained from different drying conditions are summarized in Table 2.3.
Table 2.3:

Values of rate constants and of diffusion coefficients of bananas dried at different drying conditions (ripe banana of 1 cm slabs)

<table>
<thead>
<tr>
<th>Drying temperatures (°C)</th>
<th>K (h⁻¹)</th>
<th>D (m²/s) x 10¹⁰</th>
<th>K (h⁻¹) (in literature)</th>
<th>D (m²/s) x 10¹⁰ (in literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.046</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.083</td>
<td>2.1</td>
<td>0.122 [45]</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.111</td>
<td>3.2</td>
<td>0.187 [45]</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.208</td>
<td>5.1</td>
<td>0.192 [45]</td>
<td>7.7 [91]</td>
</tr>
<tr>
<td>70</td>
<td>0.277</td>
<td>7.8</td>
<td>0.277 [45]</td>
<td>8.2 [91], [46]</td>
</tr>
</tbody>
</table>

Note: In all cases, the standard deviations in the mean K, and D were between 1-2%

for three replications

The temperature dependence of the moisture diffusivity was described with an Arrhenius type equation:

\[ D = D_o \exp \left(-\frac{E_a}{RT}\right) \quad (2.6) \]

Where \( E_a \) is activation energy (kJ/mol).

Values of \( \ln D \) at different temperatures were plotted versus \( 1/T \) for slabs of 1 cm, 2 cm. Good linearity was obtained in both cases. These plots were presented in Figure 2.3. From the slope of these lines, activation energy was derived. The values of \( E_a \)
were 39.8 (±4.6) kJ/mol, and 34.7 (± 0.073) kJ/mol for 1 cm, and 2 cm slabs respectively.

Figure 2.3: Temperature dependent diffusion coefficient of banana drying expressed as Arrhenius plots

2.3.2.3 Testing and evaluation of the model

In order to evaluate this model in predicting drying behavior of banana, experimental drying curves of banana at 30°C, 50°C, 60°C, and 70°C for 1 cm slabs were compared with those obtained by the diffusion model. In the model, the fitted values of D, K for the semilog plots were used to generate the model drying curves. The two curves
Deviation between the experimental and predicted values were calculated for data of changes of moisture versus drying times at those drying temperatures. The results of deviations will be presented as following:

<table>
<thead>
<tr>
<th>Drying temperature (°C)</th>
<th>30</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deviation</td>
<td>0.0189</td>
<td>0.0423</td>
<td>0.0001</td>
<td>0.0114</td>
</tr>
</tbody>
</table>

Note: Deviation = \([\{\text{sum} (\text{MC}_{ei}-\text{MC}_{pi})\}^2/N]^\frac{1}{2}\) \[92\]

Where MC$_{ei}$ was the moisture content obtained from experimental data at any time interval, i = 1, 2...N.
Where $MC_{ei}$ was the moisture content obtained from experimental data at any time interval, $i = 1, 2...N$.

$MC_{pi}$ was the moisture content obtained from predicted data at any time interval. $N$ was number of time steps.

The results of these deviations above, and the deviation of $D$, $K$ showed that the diffusion model could express well the mass transfer during the falling rate period of drying banana for a wide range of drying temperatures. An extremely good fit was obtained for drying at 60°C and 70°C. This agreed with expectations, because at high temperature, the rate of moisture loss was very rapid at the beginning. At this stage the evaporation of moisture from the surface controlled the rate of drying. The faster the surface moisture was deleted, the sooner the drying rate was controlled predominantly by internal diffusion.

The drying time at all temperatures also agreed very well between predicted and experimental data. The difference in drying time to a particular moisture content between the model and experimental data were 10-15 min for all drying temperatures from 30°C to 70°C.

In summary, the diffusion model gave the good fit with the experimental data. The values of moisture diffusion coefficients or constant rates, which were yielded from this model, were useful to explain the effects of different drying conditions on drying behaviors of banana. This will be discussed in the next section.
2.3.3 Effect of Process Parameters on Drying Kinetics

2.3.3.1 Effect of drying temperature on drying kinetics

Bananas were dried at 10°C intervals from 30°C to 70°C to investigate the influence of temperature on drying kinetics. The effect of temperature on drying rate was seen clearly from the results of water diffusivity in table 2.3 (referring to table 2.3 for values of D at different temperatures). Increasing temperature resulted in significant improvement of rate of mass loss, especially the initial rate. Total drying time was reduced significantly with increasing temperature. The initial drying rate and the drying time needed to obtain a 70% mass loss (wet basis) at different drying temperatures are shown in Table 2.4

Table 2.4: Comparison of initial drying rates (kg H₂O/kg DM * h) and drying times to 70% mass loss for drying bananas (1 cm slabs) at different temperatures.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial drying rate (kg H₂O/kg DM * h)</td>
<td>0.17</td>
<td>0.3</td>
<td>0.39</td>
<td>0.54</td>
<td>0.73</td>
</tr>
<tr>
<td>Drying time (min) to 70% mass loss</td>
<td>6000 ± 95</td>
<td>2520 ± 60</td>
<td>1850 ± 75</td>
<td>1320 ± 60</td>
<td>660 ± 60</td>
</tr>
</tbody>
</table>

In all cases, the standard deviations in the mean initial drying rates were between 2-4% for 3 replications. Errors quoted for the drying times are the standard deviations of the mean for 3 replications.
From this table, we can see that the drying time of banana at 70°C was twice fast as that at 60°C, three times compared to 50°C, four times that at 40°C and 10 times that at 30°C. Decreased drying time of around 10h with increasing 10°C was observed within this temperature range, except of the large difference for case of drying at 30°C.

2.3.3.2 The influence of sample thickness on kinetics of drying banana.

The drying rate in the falling rate period, which is mainly influenced by the moisture gradient in food [68], is also thickness dependent. The following section examines the effect of banana slab thickness on the kinetics of drying. Table 2.5 shows the results of rate constants and diffusion coefficients calculated from the diffusion model for 1 cm and 2 cm slabs dried at different temperatures.

Table 2.5: Rate constants and diffusion coefficients of moisture in ripe banana slabs of different thickness dried at different temperatures.

<table>
<thead>
<tr>
<th>Drying conditions</th>
<th>K (h⁻¹)</th>
<th>D (m²/s)x10¹⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 cm</td>
<td>0.11</td>
<td>3.2</td>
</tr>
<tr>
<td>2 cm</td>
<td>0.09</td>
<td>10.8</td>
</tr>
<tr>
<td>60 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 cm</td>
<td>0.21</td>
<td>5.1</td>
</tr>
<tr>
<td>2 cm</td>
<td>0.14</td>
<td>15.9</td>
</tr>
<tr>
<td>70 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 cm</td>
<td>0.28</td>
<td>7.8</td>
</tr>
<tr>
<td>2 cm</td>
<td>0.20</td>
<td>22.7</td>
</tr>
</tbody>
</table>

In all cases, the standard deviations of the mean K, D were between 1- 2% for three replications.
From Table 2.5, the thickness and temperature dependence of D can be seen clearly. The D values for 2 cm slabs were nearly 3 times greater than those for 1 cm slabs at all temperatures. This was not surprising, because the diffusion model assumed that diffusion took place from only one direction from inside slab to the surface of slabs. This assumption was okay for thin slabs, in which the edge effect (side way diffusion) was negligible. In thick slabs, the side way diffusion might occur. Taking this effect into account, the removal of moisture in thick slabs might be enhanced [93].

In the falling rate period, the concentration gradient in food matrix controls the drying rate and is temperature dependent. This led to large difference of drying rate difference between 1 cm, and 2 cm slabs within various temperatures, especially at the beginning of drying. The drying rate difference between 1 cm and 2 cm slabs is illustrated in Figure 2.5, and it can be seen that significant differences of drying rates between 1 cm and 2 cm slabs at all examined temperatures occurred in the early stage of drying (before 3 h). These differences then decreased gradually to the point when the drying rates of 1 cm, and 2 cm slabs were equal. Drying times to obtain equal rates of 1 cm and 2 cm slabs decreased with increasing temperatures.
Figure 2.5: The difference in drying rates between 1 cm and 2 cm banana slabs at various drying temperatures.

In the early stages of drying, when the fruit had high moisture content, the removal of water depended on the pathway of water from the internal sites of fruit cells toward the surface areas, where water evaporated out into the air. This pathway was thickness dependent and drying at high temperature compensated for the influence of thickness and therefore equal rates between thick and thin slabs were obtained faster.

In addition, when drying at a high temperature, a surface hardening effect occurred for the thin slabs faster than in thick slabs, due to quicker initial rate of evaporation of
moisture from the surface. This hardening effect slowed down the drying rate in the thin slabs. This in turn made the difference between the drying rate of 1 cm and 2 cm slabs decreased faster at high drying temperature than at the lower ones. This effect also could be helpful to explain why the diffusion coefficients in 1cm slabs were smaller than in 2 cm slabs.

In summary, edge effects might enhance the removal of moisture from thick slabs. A hardening effect might hinder the transfer of moisture in thin slabs after drying some hours. Both these reasons could explain why the values of D of thick slabs were higher than that of thin slabs.

2.3.3.3 The effect of initial moisture content of banana on drying kinetics.

The initial moisture content of banana harvested at different time was found to vary during this study. Bananas were dried during various months from January to November. The average moisture content (wet basis) of bananas from different months are presented in Table 2.6. A large difference between the moisture contents of January and March bananas was observed.
Table 2.6: Variations of moisture contents with different harvest seasons.

<table>
<thead>
<tr>
<th>Month</th>
<th>% MC of this work</th>
<th>% MC of literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>77.8 ± 1.2</td>
<td>77.9 [17]</td>
</tr>
<tr>
<td>March</td>
<td>71.4 ± 1.3</td>
<td>72.9 [53]</td>
</tr>
<tr>
<td>Average of other months</td>
<td>74 ± 1</td>
<td>74.4 [17]</td>
</tr>
</tbody>
</table>

Note: Errors quoted in the table are the standard deviations of the mean for 3 replications.

It was known that, the different initial moisture content in fruit resulted in great difference of initial drying rate [75, 45] and thus, the drying time. The initial moisture dependence of drying rates of Australian bananas harvested in January and March was investigated. Table 2.7 shows the results of initial drying rates and drying time of these samples dried at 40°C and 60°C (Drying to moisture content = 20 % dry basis).

Table 2.7: Drying times and initial drying rates of bananas harvested in January and March.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>40°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Month</td>
<td>January</td>
<td>March</td>
</tr>
<tr>
<td>Initial drying rate (kg H₂O/kg DM* h)</td>
<td>0.53</td>
<td>0.34</td>
</tr>
<tr>
<td>Drying time (min)</td>
<td>1575 ± 74</td>
<td>1800 ± 46</td>
</tr>
</tbody>
</table>

In all cases, the standard deviations in the mean initial drying rates were between 2-3 % for three replications. Errors quoted for drying time are the standard deviations of the mean for three replications.
The difference in initial moisture contents led to significantly different initial drying rates at both drying temperatures. This was understandable, because the higher the initial moisture content was the greater the concentration gradient established and thus, a higher driving force for mass transport would result.

From Table 2.7, it was interesting to see that different initial moisture contents resulted in longer drying times for samples dried at 40°C. Whereas drying times were nearly the same for two samples dried at 60°C, despite their being a greater initial drying rate for the banana with the higher moisture content. The increase of water diffusivity with increased moisture content has been reported elsewhere [94-96]. Thus, higher initial moisture content in food resulted in a higher drying rate, as expected. This led to rapid decrease in moisture content in the fruit, and resulted in the same drying time for both January and March samples at 60°C.

Moreover, high temperature (60°C) accelerated the evaporation of moisture near the surface better than low temperature (40°C), thus drying time could be reduced. The results of drying at 60°C agreed with the report of Sabarez [75] for drying plum of different initial moisture contents at 70°C. The author reported that at this temperature, there was very little difference in drying time between samples with different initial moisture contents. Perhaps, strong temperature dependent diffusivity of water in banana led to the difference between the two temperatures.
2.3.3.4 The influence of maturity of banana on drying kinetics

There were many reports of changes in structure (intercellular space, cell wall) [24, 25, 35], permeability of membrane [23, 97-99], chemical compositions (starch, sugar) [19, 20, 25, 100, 101] and especially moisture content [1, 19-22, 36, 79, 102] in green and ripe banana. It was therefore worthwhile to investigate the drying kinetics of banana of different maturity. Green banana and ripe ones of the same hand (given six days more to mature) were dried under the same drying conditions (temperature, thickness, and humidity and air velocity).

Mass loss of green and ripe bananas as a function of drying time was very similar for all drying temperatures and thickness. Their drying rates and diffusivities were also seen to be similar at the same drying conditions. (Figure 2.6 is presented as an example).

Figure 2.6: Drying rates of green and ripe banana (1 cm and 2 cm slabs) dried at 70°C
The values of K, and D (calculated from the diffusion model) of green and ripe samples under different drying conditions are presented in Table 2.8.

Table 2.8: Rate constants and diffusion coefficients of green and ripe banana dried under different drying conditions.

<table>
<thead>
<tr>
<th>Drying conditions</th>
<th>K (h⁻¹)</th>
<th>D (m²/s)×10¹⁰</th>
<th>K (h⁻¹) (literature)</th>
<th>D(m²/s)×10¹⁰ (literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C, 1 cm</td>
<td>green</td>
<td>0.14</td>
<td>3.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ripe</td>
<td>0.11</td>
<td>3.21</td>
<td>0.187 [35]</td>
</tr>
<tr>
<td>60°C, 2 cm</td>
<td>green</td>
<td>0.13</td>
<td>14.75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ripe</td>
<td>0.14</td>
<td>15.87</td>
<td>0.098 [35]</td>
</tr>
<tr>
<td>70°C, 1 cm</td>
<td>green</td>
<td>0.30</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ripe</td>
<td>0.28</td>
<td>7.8</td>
<td>0.277 [35]</td>
</tr>
<tr>
<td>70°C, 2 cm</td>
<td>Green</td>
<td>0.18</td>
<td>20.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ripe</td>
<td>0.202</td>
<td>22.74</td>
<td></td>
</tr>
</tbody>
</table>

In all cases, the standard deviations in the mean K, D were between 2-3 % for three replications.

The effect of structure, physical characteristics, and chemical composition while a complex combination, overall resulted in the same general drying kinetics for green and ripe bananas. Green banana contains a large amount of starch (20% [20] and less moisture content compared to ripe [19, 21, 79]). It is less porous than ripe banana as ripe banana has a more open cell structure (cell wall thinning, increase of intercellular space, loosening of cells [25], degradation of starch). Green banana has a higher viscosity [23], and the cell membrane is less permeable than that of the ripe one [97-
From all these factors, theoretically, we can expect the drying rate of ripe banana to be faster than that of the green one. However, in reality, from this study, the rates were found to be nearly the same. This agreed well with report of Garcia et al [47]. However, Jayaman and Das Gupta [103] reported that the rate at which green banana dehydrated at 23°C, 80-90 % RH%, was significantly higher than that of ripe banana. Perhaps, an explanation is that a large amount of sugar in ripe banana (from starch degradation) results in lowering of water mobility in ripe banana. This compensation resulted in equal drying rates for green and ripe bananas. Many authors [35, 56, 73, 104-107] have reported that the increase of sugar in fruit reduces water diffusivity during dehydration. This matter will be discussed further in chapter three on osmotic dehydration of banana. Evidence that a large amount of sugar exists in ripe banana is showed in Figure 2.7. Green banana was still white after drying, and was very crisp due to high level of starch; in contrast, a high sugar level in ripe banana made it turn brown after drying.

Figure 2.7: Color of green and ripe dried banana slabs (Drying was carried out at 60°C)
In conclusion, it is not only moisture content and drying conditions that determine drying rates but also the composition of fruit at different maturities which significantly affects water diffusivity during dehydration.

2.4. CONCLUSION

From the proposed model, it could be seen that the solution to Fick’s diffusion equation for an infinite slab was simple and useful to model the drying kinetics of drying banana slabs. The deviation between predicted and experimental moisture contents during drying showed that good a fit was obtained at all drying temperatures. Perhaps, under these drying conditions, very little non-moisture loss was observed.

Temperature dependence of diffusivity followed an Arrhenius type equation with a high correlation coefficient \((R^2 = 0.99)\), and the apparent moisture diffusivity obtained in this work agreed with data reported in literature.

Among the examined drying conditions in this study, it was clearly that the temperature was the most important parameter influencing drying kinetics of banana. 60°C was considered the most suitable drying temperature in terms of production cost, as drying at this temperature resulted in a suitable rate with little non-moisture loss.
The difference in drying rates for banana slabs of different thickness showed that drying banana followed mainly the internal moisture transfer of the falling rate period, in which water diffusivity depended upon both temperature and distance.

Initial moisture content varied with bananas of different harvesting seasons. The large difference in initial moisture content (over 5% wet basis) could strongly affect drying rates. However, this effect was only clearly observed at low temperature (40°C). At a higher drying temperature this was not seen, since temperature dependence of diffusivity was stronger than the concentration dependence.

Mass loss at all drying conditions between green and ripe banana was very similar. This showed that mass loss was not influenced much by fruit morphology. However, chemical changes, especially significant rise in the amount of sugar in ripe banana can contribute to reducing the rate of mass loss of ripe banana. This compensated the more open structure of ripe banana although this structure might favor an increased drying rate for ripe banana.
CHAPTER THREE

OSMOTIC DEHYDRATION OF BANANA AND ITS EFFECTS ON SUBSEQUENT AIR-DRYING
3.1 INTRODUCTION

Osmotic dehydration of a foodstuff is a process of water removal from a foodstuff into an osmotic medium. This involves the immersion of food in a concentrated solution (e.g. concentrated sugar or salt solution). The driving force for the diffusion of water from the food is the higher osmotic pressure of the concentrated solution [35] compared with the lower concentration of sugar in the foodstuff [56].

Fruit tissue is generally composed of many cells, containing water and natural solutes of fruit such as sugar, organic acids, mineral substances, and other chemical substances [108]. Free spaces or intercellular spaces are located among these cells. When fruit is put in the sugar solution, water inside fruit cells will migrate out and gradually diffuse from fruit tissue into the osmotic medium. It might be expected that there is not any leakage of solute from the solution into the food, as the cell wall of food acts as a semi-permeable membrane [56]. However, the membrane is only partially selective [104]. Therefore sugar of osmosis agent diffuses from sugar solution into the fruit tissue and accumulates in the intercellular spaces [109]. Thus, osmotic dehydration is a simultaneous water and solute diffusion process.

In addition, there may be the leaching of food's own solutes such as sugars, minerals, vitamins and organic acids out into the osmotic medium [57]. The leaching of food solutes is quantitatively negligible compared to the water transfer into the solution and solute transfer from the solution into the fruit. Figure 3.1 describes the general mass transfer phenomena of osmotic dehydration of fruit.
Mass transfer during osmosis is affected by process variables such as temperature, concentration of osmosis agent, sample size, and agitation. In addition, the biological microstructure of fruit plays an important role in both water and solute transport. In recent years, osmotic dehydration has been applied to improve product quality for foodstuff.

Osmotic dehydration has been applied to a wide range of foodstuffs such as fruits, vegetables, meat [110], and eggs. Most reports on osmotic dehydration of fruits in the
literature were studies of apples [57, 104, 108, 111-117]. Other fruits studied have been peach, apricot [109, 116, 118, 119]; cherries, grapes and plums [105, 115, 119-121], blueberries [122, 123], pineapple [107, 109, 124-127], strawberries [111, 128], mango [129], kiwi and papaya [57, 130, 131]. Osmotic dehydration of vegetables such as potato, pea, onion, and white beans have also been reported [106, 108, 132-139].

Preservation of food by osmotic dehydration as a pretreatment prior to air-drying has several advantages over conventional dehydration methods. Firstly, the initial rate of water removal by osmotic dehydration is very fast. For example, Bongirwar and Sreenivasan [61] reported a 50 % mass loss after 3 hours of osmotic dehydration of sliced banana with 70% solution sucrose, at 50°C. This occurred without a phase change in the products. As a consequence, the natural cell structure was preserved [140]. Heat damage in osmosed samples is generally less than that in air-drying at the same dehydration temperature. For example, the porosity of air-drying samples increases during drying, but in osmosis the porosity of the sample is nearly constant [140]. The lower level of heat damage results in the retention of natural color, without chemical treatment needed prior to conventional drying. This is understandable, since the presence of sugar on the surface of osmosed samples inhibits oxygen, and hence enzymatic-browning reactions will be reduced compared to air-dehydrated fruit [139]. The loss of fruit volatiles is also decreased, even under vacuum conditions [45, 141]. The effect of osmotic dehydration on retaining volatiles during drying has been reported by many authors [35, 104, 106, 125, 129, 134, 138, 139, 142-144].
During osmotic dehydration at least two flows of water and solute act at the same time. Their influences on mass transfer (i.e. water loss and solute gain) depend on the nature of the fruit and the operating conditions. The former consists of properties of fruit (i.e. permeability of cell and porosity of fruit tissue) and contents of solute in fruit (i.e. sugar contents). The latter are process temperature, concentration, and kinds of osmotic agents, applied pressure during osmotic process, agitation, thickness of slab, pretreatment of fruit and immersion time. Temperature and concentration of sugar solution are the most important parameters in controlling the rate of water loss and solute uptake. Most previous studies [105, 117, 119, 122, 127, 145-148] have focussed on these two operating conditions, because a high osmotic rate would make the process more practical. However, the quality of the products is also paramount. Therefore, many authors focussed their studies on optimising the conditions for osmotic dehydration to improve the quality of products. For example, the optimal conditions for improvement of color in the final product (decreasing the browning) were reported by Grabowski et al [105] for dried grape, Torreggiani et al [120] reported the influence of osmotic time on color, organoleptic characteristics, and stability of products’ nutrients during storage for cherries. Texture was improved by optimising the concentration of syrup as well as using a suitable osmotic agent. This was reported for apple [104], potato [135], and blueberries [123, 149]. Decreased shrinkage in osmosed products by using concentrated syrup was reported for strawberries [111, 136], and potatoes [135].

Improving the rate of water removal in osmosis by pretreatment of samples prior to osmotic dehydration (especially for skin fruit) has also been reported. For plums
soaking them in an emulsion of aqueous potassium carbonate and Voullaires oil [121] was tried, whilst grapes have been dipped in ethyl oleate at 80°C [105]. Blanching is another pretreatment and has been reported for osmotic dehydration of strawberries [128]. Other trials by Camirand et al [150], and Paer and Richberg [151], showed results consistent with this. These studies reported the better retention of color for pretreated-osmotic fruit after drying.

Most studies on osmotic dehydration were carried out under atmospheric pressure. Decreasing pressure in processing leads to quicker dehydration but does not influence solute uptake [108]. Some authors studied the effect of pressure on the kinetics of water transfer during vacuum osmotic dehydration [108, 114, 148, 152]. They showed that vacuum osmotic dehydration intensifies the capillary flow leading to a significant increase in water transfer compared to that obtained at atmospheric pressure, especially for fruit and vegetables with high porosity such as pineapple, potato, apple. The effects of osmotic dehydration on the subsequent thermal dehydration have not been reported widely in literature. Only some studies of this aspect were reported for apple, mango, pea, pineapple and blueberries [106, 107, 108, 122, 129].

Previous authors have focussed their studies on modelling the mass transfer process in osmotic dehydration of banana. Some authors have proposed empirical models to predict water loss during osmotic process [55-58]. Only one report on air-drying behavior of fresh and osmotically dehydrated banana slices [45] was found. These studies did not investigate the influence of different osmotic agents on mass transfer. So far, no report
has been found in the literature about the relationship between maturity of banana and its effect on the course of net mass loss during osmotic dehydration.

In this work, the aim of the studies will be focussed on:

i) The effect of osmotic agent on both water transport and solute uptake during osmotic dehydration of banana

ii) The alteration of fruit micro-structure during ripening was considered as an important factor, since it would have a significant role on the net change of water removal and solute uptake. In addition any leakage of solute in fruit in osmotic dehydration of banana could be detrimental as far as organoleptic or nutritional quality is concerned.

iii) The optimisation of osmotic conditions (temperature, concentration of syrup, and type of sugar) for the improvement of dried banana quality.

iv) The effect of osmotic dehydration on subsequent air-drying.

A better understanding of the complex effects of process conditions, and the nature of banana will help to improve quality of dried banana using osmotic dehydration as a means of preconcentration.
3.2 EFFECT OF EXPERIMENTAL PARAMETERS ON OSMOTIC DEHYDRATION OF BANANA

3.2.1 Materials and Methods

*Fruit*

Banana used was Cavendish variety, grown in North Queensland. They were bought from a local market at yellow and green skin stage of maturity, and were stored at room temperature (20°C-25°C) for some days during each set of experiments.

*Initial moisture content analysis.*

Two methods were applied to analyse the initial moisture content. In the first one, bananas were peeled, weighed (250 g banana) and cut into 1 cm slices. Then they were dried in a fan-forced oven (Labec, Sydney) at 60°C until a constant weight was obtained. Usually it took 72 hours to reach constant weight if only one side was contacted to hot air (samples were put on aluminum foil). If both sides were contacted to hot air, drying time took 54 to 60 hours depending of the initial moisture content of bananas. In this case, mesh trays were used to hold the samples. The drying chamber was equipped with an automatic temperature controller. The airflow was turbulent.

The second method was vacuum drying at 60°C, for 48 h [55] over a magnesium sulphate desiccant. The initial moisture content was expressed in percentage of wet basis. Each experiment was performed in triplicate and the means were used to interpret data.
Osmotic dehydration.

Sucrose, commercially graded white sugar (CSR) and glucose (dextrose monohydrate) were used for preparing osmotic syrups. They were weighed using an electronic balance accurate to 3 decimal places. The volume of water was measured with a measuring cylinder. Concentration of syrup was expressed in percentage (w/w). The ratio between fruit and syrup was 1:20 to prevent significant variation of concentration during osmosis.

Mass loss determination

The banana was peeled, weighed (50g) and cut into 1cm slices. Slices of banana were placed in glass beakers containing syrup of desired concentration. The beakers were put in a thermostated water bath. After osmotic dehydration for various immersion times, samples were removed from the syrup. They were immediately rinsed gently with water to wash adhering osmotic solution from the surface. They were then touched dried very gently by tissue, and reweighed.

Percentage mass loss was calculated as

\[ \% \text{ Mass loss} = 100 \times \left( \frac{m_0 - m_t}{m_0} \right) \text{ (g/100g wet basis)} \]

Where \( m_0 \) = initial mass of banana before osmosis.

\( m_t \) = mass of banana after being osmotically dehydrated for a set period of time

Temperatures were carried out in the range of 30°C, 40°C, 50°C and 60°C. Glucose and sucrose concentrations were 30%, 40%, 50%, and 60%.
**Solute uptake determination**

Fresh banana (200g) and osmotically dried banana (from 200g fresh banana) of the same hand were dried in a fan forced oven (Labec) at 60 °C until a constant weight was obtained. The percentage of solid uptake was calculated as

\[
\text{% Solid uptake} = 100 \times \frac{m_{od} - m_d}{m_o} \text{ (g/100g wet basis).}
\]

Where

\( m_d \) = mass of thermally dried fresh banana (at constant weight).

\( m_{od} \) = mass of osmotically and thermally dehydrated banana at constant weight,

\( m_o \) = initial mass of fresh banana.

### 3.2.2. The Influence of Temperature and Concentration of Osmotic Agents

The net mass loss (i.e. the combination of water loss and solute uptake) during osmotic dehydration was investigated at 30, 40, and 60°C for both sucrose and glucose syrups of 30, 40, 50 and 60%. The results are summarized in Table 3.1. It could be seen that the mass loss from osmotic dehydration using both high concentration and high temperature was as fast as that of air-drying at the same drying temperature. For example, comparing osmotic dehydration (at 60°C, using 60% sucrose syrup) with air-drying at 60°C, the values of percentage mass loss after osmotic and air-drying in 3h, 5 h and 7 h were very similar (mass loss in air-drying were 34, 46, and 54% respectively).
At constant temperature, mass loss from osmotic dehydration of banana with both sucrose and glucose increased with sugar concentrations. Moreover, from table 3.1, considering each concentration, it can be seen that the rate of mass loss was temperature dependent. Significant increase in mass loss was observed at 60°C ($P < 0.001$, statistically different at all levels of significance). A comparison of the effect of temperature and concentration on mass loss will be presented in the following sections.

Temperature had a greater effect on mass loss than concentration. This trend is illustrated in Figure 3.2 for glucose syrup osmotic dehydration. The same trend was observed for sucrose osmosis.

Figure 3.2a shows the difference in mass loss using 30% and 60% glucose solution for 3 h at different temperatures. Figure 3.2b shows the difference in mass loss between immersion temperature of 30°C and 60°C using glucose solution of different concentrations, for 3 h. The results of osmotic dehydration for 3 h are presented as an example. Similar trends were found for 5 h and 7 h immersion.
Table 3.1: Mass loss during osmotic dehydration of banana (g H₂O/100g wet basis)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass loss (g H₂O/100g wet basis)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>40</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration</td>
<td>Time (h)</td>
<td>Sucrose</td>
<td>Glucose</td>
<td>Sucrose</td>
<td>Glucose</td>
<td>Sucrose</td>
</tr>
<tr>
<td>(% w/w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>13.3</td>
<td>12.5</td>
<td>15.5</td>
<td>13.6</td>
<td>22.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>15.4</td>
<td>14.6</td>
<td>19.9</td>
<td>17.4</td>
<td>27.4</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>19.3</td>
<td>17.8</td>
<td>24.2</td>
<td>20.2</td>
<td>34.9</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>26.3</td>
<td>23.2</td>
<td>31</td>
<td>30.7</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>3</td>
<td>17</td>
<td>15.9</td>
<td>19.4</td>
<td>17.8</td>
<td>28.6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>20</td>
<td>19.3</td>
<td>23.6</td>
<td>22.2</td>
<td>35.6</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>24.1</td>
<td>23.2</td>
<td>29.6</td>
<td>27.4</td>
<td>44.3</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>30.2</td>
<td>30.1</td>
<td>37.4</td>
<td>35.9</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>3</td>
<td>19.7</td>
<td>18.4</td>
<td>21.7</td>
<td>19.4</td>
<td>32.9</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>23.4</td>
<td>21.9</td>
<td>27.8</td>
<td>24.3</td>
<td>40.7</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>30</td>
<td>28.3</td>
<td>35.4</td>
<td>32.3</td>
<td>47.5</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>36.7</td>
<td>34.5</td>
<td>46</td>
<td>40.3</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>3</td>
<td>20.2</td>
<td>19.1</td>
<td>25</td>
<td>21.4</td>
<td>36.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>27.8</td>
<td>27.4</td>
<td>33</td>
<td>29.8</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>33.9</td>
<td>32.6</td>
<td>37.1</td>
<td>38.3</td>
<td>54.5</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>39.3</td>
<td>37.1</td>
<td>48.6</td>
<td>45.6</td>
<td>-</td>
</tr>
</tbody>
</table>

(In all cases, the standard deviations in the mean % mass loss were between 1- 2% for three replications)
Figure 3.2: The comparison of the mass loss difference due to changing temperature (from 30°C to 60°C) or concentration of glucose (from 30% to 60%), for 3 h osmotic dehydration of 1 cm banana slabs.

Note: dC: From 30% to 60% solution syrup.

dT: From 30°C to 60°C

Clearly, the increased mass loss due to increased concentration from 30% to 60% for all temperatures was found to be less than that for increased temperature from 30°C to 60°C for all concentrations. This seemed to disagree with the study of osmotic dehydration of banana of Poharkar et al [54]. They found that an equal increase in mass loss was obtained if increasing 10°C (at constant concentration) or an increase in 10°Brix (sucrose) (at constant temperature). Ramaswamy et al [122] studying
osmotic dehydration of blueberries came to a similar conclusion. However, the following reasons might support the results of the current work.

The change in concentration had two competing effects. Increasing concentration resulted in increasing osmotic pressure, as well as viscosity of syrup. The former enhanced diffusion of water, but the latter slowed the penetration of solute, as mobility of the solute decreased at high concentration syrup. This might influence the external mass transport rate (at the product/solution interface). By contrast, an increase in temperature enhanced osmotic pressure and permeability of fruit cell wall, but decreases viscosity. All of these factors favored mass transfer (both water and solute) during osmotic dehydration.

Moreover, Figure 3.2b illustrated that increased temperature had a greater effect at higher syrup concentration. This might be because the more concentrated the sugar solution was, the more its viscosity increased at the same temperature, especially at low temperature. An increase in temperature had considerable influence on the viscosity of concentrated syrup more than that of low content syrup. Buckle et al [127] reported a similar case for osmotic dehydration of pineapple. Some data from Table 3.2 on the changes of viscosity of sucrose with various concentrations and temperatures might support the discussion above. The data was consistent with the hypothesis.
Table 3.2: Data of viscosity of sucrose (unit of viscosity is millipoise) [153]

<table>
<thead>
<tr>
<th>Sucrose solution (% w/w)</th>
<th>20</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>15.1</td>
<td>340.1</td>
</tr>
<tr>
<td>60°C</td>
<td>8.1</td>
<td>98.7</td>
</tr>
</tbody>
</table>

In air-drying, mass loss is considered as water loss. But the overall mass loss in osmotic dehydration is a combination of water loss and solute uptake. The variation in solute uptake with experimental conditions is shown in Table 3.3 for osmotic dehydration 5 hours.

Table 3.3: The Influence of Temperature and Concentration on solute uptake during Osmotic Dehydration of Banana for 5 Hours. (% Solute uptake = g/100g fresh banana)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Concentration (% w/w) of osmotic syrup</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40</td>
</tr>
<tr>
<td><strong>Sucrose</strong></td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td><strong>Glucose</strong></td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>60</td>
</tr>
</tbody>
</table>
The influence of temperature and concentration of sugar on solute uptake was similar to that for mass loss: increasing temperature generally accelerated solute uptake at the same concentration. This is understandable, because temperature accelerates not only water flow but also the solute flow. However, there were some exceptions at 40°C for sucrose osmosis. This meant that at constant concentration, increased temperature did not always have a positive effect on solute uptake. The same phenomenon had been reported for the osmotic dehydration of pineapple, and blueberries [118, 122, 127]. This matter will be discussed in section 3.2.2.

In addition, it can be seen from Table 3.3 that at low temperature (30°C) increased concentration did not always have a positive effect on solute uptake. This might be due to an increase in viscosity of high concentration syrups, which inhibited the movement of solute. Moreover, highly viscous syrups might initiate crystallization of sugar on the surface of fruit at low temperature, which also hindered uptake of sugar. The same phenomenon was observed for osmotic dehydration of blueberry [122]. In addition, Mauro and Menegalli [55] reported a decrease in effective diffusion coefficients of sucrose in syrup concentration 68.2% in comparison with that of syrup concentration 47.2%, at 30, 40 and 50°C.

Besides the relationship between solute uptake and experimental conditions, the relationship between solute uptake and immersion time has been of much interest [54,
A better knowledge of this matter is useful, because it helps control better the level of solute, which influences the final quality of osmotic-air-dried fruit. This matter will be discussed in the following sections. Figure 3.3 shows the changes of solute uptake from sucrose and glucose osmosis for different immersion times. The result of 50 and 60 % syrup at 30 and 60 °C are presented as the examples to examine the temperature dependence of increased uptake with the length of osmotic process. The results of other syrup concentrations had the similar trends.

Figure 3.3: Comparison the changes of net sucrose and glucose uptake with immersion time from osmotic dehydration of banana at 30 and 60°C using 50 and 60 % syrup
At 60°C a reasonably linear increase in uptake with immersion time was found for both sucrose and glucose osmosis. By contrast, a non-linear trend in solute uptake versus different immersion time was observed at other temperatures (only the results at 30°C are presented as an example). There were also two trends in the variation of solute uptake depending on whether glucose or sucrose was used. At 30°C, from 3 h to 5 h, glucose uptake dramatically increased, and dropped thereafter to 7 hours. The opposite trend was seen for sucrose uptake. Perhaps greater leaching out of solute from the banana might explain the drop in net solute uptake (this matter will be discussed further later).

In general, at 60°C, the rate of solute uptake was accelerated (due to loss of selective permeability, decrease of viscosity, decrease in solubility of sugar, and increased effective diffusion coefficient of solute) which would compensate for the influence of any leaching. As a result, increased solute uptake was linear for increased immersion times at 60°C. A fluctuation in solute uptake with increased immersion time has been reported by Nsonzi and Ramaswamy [122] for blueberries at various combinations of temperatures and concentrations. A similar case was observed in osmotic dehydration of apple [104]. In addition, Lazarides and Mavroudis [135] reported that solute uptake was proportional to immersion time during osmotic dehydration of potatoes only at 50°C. At other temperatures, great variations in solute uptake were observed.

In conclusion, the effects of temperature, concentration and type of sugar on rate of solute uptake with processing time presented a complex picture. This strongly depended on the relative importance of the leaching of solute from the fruit and the
uptake of sugar at the particular experimental condition (namely at different temperatures). Therefore, a linear relationship between solute uptake and process time could be obtained only at specific experimental conditions. This point is very important in terms of quality of osmotic dehydrated fruit, since both high solute uptake and high leakage of fruit solute do not benefit final fruit quality.

3.2.3 The Influence of Type of Sugar

In general, as shown previously in Table 3.1, net mass loss during sucrose osmosis was faster than using glucose across the full range of concentrations and immersion times at 30 and 40°C but not at 60°C. The net mass loss is equal to the water loss minus the solute uptake (if leakage is negligible). Therefore, to examine the temperature dependence of net mass loss during osmosis using these sugars, it was necessary to examine the changes in water loss and solute uptake at different temperatures.

Glucose uptake was greater than sucrose uptake across the full range of temperatures and concentrations examined in this work (table 3.3). This may be due to different molecular weight and size, solution viscosity, and the solubility of the two sugars.

Sucrose is a bigger molecule than glucose; thus sucrose might uptake less than glucose, due to size exclusion. Large-molecular-size solutes seem to be “membrane-impermeable” [132]; therefore, the level of sugar uptake is inversely related to the size
of the sugar molecule. [112, 155]. This matter has been discussed by many authors [106, 112, 124, 155-157].

On the other hand, the molecular weight of the solute also influences the level of uptake. Glucose has a smaller molecular weight than sucrose, therefore for the same syrup concentration (% weight); glucose has a greater molar concentration than that of sucrose. Thus glucose solution has a greater osmotic pressure than that of sucrose, and as a consequence, glucose uptake will be more than sucrose uptake.

Moreover, at different osmotic conditions, the different solution viscosity between two sugars also influences the amount of solute uptake of these sugars. For example at constant temperature, increasing concentration may inhibit sucrose uptake, but not glucose uptake due to sucrose being more viscous than glucose at the same concentration [153].

In summary, the competing influence of osmotic pressure gradient change, solution viscosity and other effects might explain some of the anomalies the data for sucrose uptake.

Results for water loss during osmotic dehydration for 5 h using sucrose and glucose syrup at different concentrations and temperatures are presented in Table 3.4.
Table 3.4: Water loss during Sucrose and Glucose osmosis for 5 hours

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Concentration of osmotic syrups (% w/w)</th>
<th>Water loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>30</td>
<td>Sucrose</td>
<td>16.8</td>
</tr>
<tr>
<td></td>
<td>Glucose</td>
<td>16.3</td>
</tr>
<tr>
<td>40</td>
<td>Sucrose</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>Glucose</td>
<td>20.0</td>
</tr>
<tr>
<td>60</td>
<td>Sucrose</td>
<td>29.5</td>
</tr>
<tr>
<td></td>
<td>Glucose</td>
<td>37.0</td>
</tr>
</tbody>
</table>

In all cases, the standard deviations in the mean % water loss were between 1-3% for 3 replications.

It can be seen that the extent of the concentration dependence of water loss at 30°C and 40°C was the same for both osmotic agents. At 60°C, water loss from glucose solutions was much greater than that of sucrose (P<0.05 for the entire range of examined concentrations). The possible reason was at high temperature, the hydrolysis of sucrose might become significant. The rate of the hydrolysis of sucrose at 60°C is more 10 times faster than that at 40°C [158-159]. This led to a decrease of sucrose content and a concurrent increase in glucose content in the examined sucrose syrup.
This would result in greater solute uptake (due to increased osmotic pressure) and less water loss. This was because in the process, equilibrium was reached when the water activity of fruit and syrup become equal [55, 124, 127]. Both water loss and solute uptake could lead to decreasing water activity. Hence, if solute uptake increased, water loss would decrease [104, 127, 131, 135, 145, 160]. This was due to the antagonistic effect of the counter current flows (water and solute).

The comparison of the changes of water loss and solute uptake at different temperatures might be helpful to explain why the net mass loss of glucose was greater than that of sucrose at 60°C. The changes of water loss and solute uptake during sucrose and glucose osmosis at different temperatures are presented in Figure 3.4 for a 40 % syrup. The trend was similar for other concentrations examined in this work.

Figure 3.4: Changes in water loss and solute uptake as a function of temperature.

(Note: Osmotic dehydration for 5 hours, syrup 40 %)
From this figure it can be seen that the increase in solute uptake with increased temperature for sucrose was more than that for glucose. On the other hand, the difference between sucrose and glucose uptake at 60°C was lower than that of other temperatures. The hydrolysis of sucrose at 60°C might explain this (i.e. because the formation of glucose from the hydrolysis of sucrose).

In contrast, water loss differences using sucrose and glucose were small at 30°C and 40°C, whereas at 60°C water loss between the two sugars differed clearly. Thus, looking at the combined trend of water loss and solute uptake; it could be seen that at 30 and 40°C net mass loss with sucrose were greater than that with glucose due to water loss being similar for both syrups, and sucrose uptake was less than glucose uptake. Whereas, at 60°C water loss during glucose osmosis increased more considerable than that for sucrose osmosis, but the increased glucose uptake was less considerable than that of increased sucrose uptake. As a result, the net mass loss of glucose was greater than that of sucrose at 60°C.

In conclusion, due to different physical characteristics of sucrose and glucose, they responded differently to variations in osmotic conditions. The difference in solute uptake of these sugars was strongly dependent on experimental conditions. The different responses of water removal and solute uptake with increasing temperature was due to the antagonistic effect between counter-current flows of water and osmotic agent [135].
3.2.4 The Effect of Banana Maturity on Osmotic Dehydration.

Besides the effect of experimental variables, the microstructure of the fruit (i.e. tissue properties or cellular arrangement) had a strong impact on transport properties in fruit during osmotic dehydration. During ripening, a change in cellular organization of banana has been observed [23, 25]. Softening of ripe banana results from chemical changes (i.e. carbohydrate metabolism) [23, 25] which in turn has an important role in cell wall degradation. This leads to great changes in intercellular spaces, and the leakage of solute from fruit. Osmotic dehydration of green and ripe bananas (bananas from the same hand of the green one were left to ripen for an additional six days) were carried out to clarify the role of fruit microstructure on solute uptake during osmosis (Osmotic dehydration at 30°C, using 60% glucose solution). The results are shown in Table 3.5

Table 3.5

Solute uptake of green and ripe banana osmosed at 30 °C with 60 % sucrose solution.

<table>
<thead>
<tr>
<th>Immersion time (hours)</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solute uptake(G/100g fresh banana)</td>
<td>Green</td>
<td>2.3</td>
<td>4.6</td>
<td>6.5</td>
<td>5.8</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>Ripe</td>
<td>1.1</td>
<td>1.3</td>
<td>2.4</td>
<td>2.9</td>
<td>2.9</td>
</tr>
</tbody>
</table>

In all cases the standard deviations of the mean solute uptake were between 1-3% for 3 replications)
Increased cell membrane permeability during ripening of banana has been reported by some authors [97, 161, 162]. It is thus expected that the rate of solute uptake during osmotic dehydration would be more rapid for ripe samples than for the green ones. As increased permeability means selectivity of cell membrane decreases, which favors diffusion of osmotic solute. However, the results from Table 3.5 showed that solute uptake from green banana were much more (up to 3.5 times) than that of ripe banana. There was clearly another factor, which controlled the level of sugar uptake into tissues of ripe banana, other than the role of cell membrane. There were two possible answers for the lower solute uptake in ripe banana than in the green one.

The increased sugar content in ripe banana might be the obvious influence. Sugar content of ripe banana increased significantly due to the degradation of starch during the ripening process (from 1.8 % total sugar to 19% from green to ripe banana [25]). When the sugar content in fruit increased, the rate of solute uptake drops during osmotic processing due to the decreased osmotic pressure between the fruit and the osmotic agent. Another possible reason might be the influence of structure changes in fruit tissue between green and ripe banana.

Micro-structural studies showed that the intercellular spaces play an important role in mass transport [108, 163, 164]. When solute penetrates into fruit, solute will occupy these intercellular spaces; and this helps to prevent leakage of solute inside the cell. If there is any decrease in cell size, which makes the intercellular spaces expand, then loss of solute occurs. As a result, a decrease of net solute uptake will be observed. Prabha and Bhagyalakshmi [25] reported this phenomenon in studies of
microstructure in ripe banana. The leakage of solute in osmotic dehydration of ripe banana might thus be the reason for higher solute uptake in green osmosed banana than that of ripe.

3.2.5 Conclusions on the Optimal Conditions for Osmotic Dehydration of Banana

From the results of all the studies above, general conclusions for the optimisation of osmotic dehydration of banana might be given:

1) Faster water removal, and minimal net solute uptake required a high temperature.
2) Sucrose uptake was generally less than that of glucose, whereas the rate of mass loss was higher for sucrose.
3) Loss of fruit solute during osmotic dehydration of ripe banana could affect the amount of solute uptake.

In order to take advantage of osmotic dehydration prior to subsequent thermal drying, following criteria should be met: (i) osmotic dehydration achieves significant water removal in the shortest time; but (ii) that osmotic dehydration enhances quality of final product. The combined effects of temperature, sugar concentration, immersion times, and type of sugar should be taken into account. The optimal
condition for osmotic dehydration of banana was found to be at 30°C with 60%, sucrose solution, for 4 hours.

Although high temperature favors fast water removal, a number of limitations for its use exist. Enzymatic browning, shrinkage, softening of tissue, decreases of nutrition content (for example vitamin C) and flavour deterioration all occur with higher immersion temperature. Therefore, 30°C might be the most suitable temperature for osmotic dehydration of banana in terms of maintaining fresh volatile flavours, and color. The effect of osmotic dehydration on the improvement of colour for dried banana is illustrated in Figure 3.5.

Figure 3.5: Comparison of the colour of dried banana with and without osmotic dehydration prior to air-drying.
Low concentration syrup led to substantial loss of solutes compared with higher concentration. In addition, heavy syrup inhibits polyphenoloxidase that causes browning [45, 140]. Moreover, high concentration benefits the retention of volatile flavors [165, 166]. By contrast, at low temperature, 30 °C, a 60 % w/w syrup did not give a higher uptake than any other concentration. Minimal solute uptake into sample was preferred. This reduced the decreased drying rate on subsequent air-drying (this will be discussed in the next section) as well as the sweetness of product.

Four hours immersion was optimum, because rate of mass loss was fast in the first hours of the osmotic process. Moreover, prolonged immersion time would lead to the loss of solute, nutrients and volatiles, and resulting in softening of the fruit, which prolonged time for thermal drying thereafter. Under the same experimental conditions, the ratio of water loss to solute uptake was a maximum at 4 hours osmotic immersion. Thus, 4 hours immersion was sufficient to obtain around 25 % mass loss, with a minimum of solute uptake, and minimal fruit nutrient loss.

3.3 THE INFLUENCE OF OSMOTIC DEHYDRATION ON SUBSEQUENT AIR-DRYING OF BANANA.

3.3.1 Introduction

Depending upon the osmotic conditions, the influence of this preconcentration on subsequent air-drying differs. The effect of osmotic dehydration on subsequent air-
drying of banana was investigated for osmosed green banana (8 hours and 16 hours),
and osmosed ripe banana (the same hand of the green one, 10 hours) in 60 % sucrose
solution, at 30°C. On the other hand, osmotic-air-dried banana using glucose osmosis
was compared to sucrose osmosis under the same condition. These experiments were
carried out to confirm the influence of level of solute uptake on subsequent air-drying
of banana. This was the reason why prolonged periods of osmotic dehydration were
used as a pretreatment, rather than the four-hour optimum time. The purpose here was
to maximize the range of solute uptake.

3.3.2 Experimental Method

Fresh banana slabs were osmotically dehydrated at 30°C, with a 60 % syrup for the
different immersion times (8 hours, 10 hours, and 16 hours). 250 g osmosed banana
was used for each experiment. They were then subjected to air-drying at 60°C using
an automatic drier (refer to experiments in 2.2). Drying was carried out until a
constant weight was obtained. From the data of mass loss versus drying time, the
moisture content was calculated as:

\[
\text{Moisture content} = \frac{(m_{od} - m_d)}{m_d} \ (\text{kg H}_2\text{O/kg DM})
\]

Where \( m_{od} \) was the mass of osmotic-air-dried banana at time \( t \), and \( m_d \) was dry mass
of fresh banana.

Drying rates of air-dried banana and that of osmotic-air-dried banana were calculated
from transient drying data. The drying rate was the slope of the plot of moisture content versus time (refer to method of section 2.2).

### 3.3.3 Results and discussion

The drying rate curves for fresh and osmosed banana slabs are presented in Figure 3.6. From Figure 3.6, the subsequent air-drying rate was much faster for the untreated samples. The reason for this appeared to be the influence of solute uptake during osmotic dehydration on subsequent air-drying. The values of solute uptake were 5%, 3.1% and 5.6% for 8 h-osmosed, 10 h-osmosed and 16 h-osmosed samples respectively. The competing effect of solute uptake and the leakage of solute from the ripe banana might explain why there was less solute uptake of 10 h-osmosed samples than of others.

Solute uptake resulted in decreased water activity and increased viscosity in fruit. Both of these factors might lead to decreased water movement, and as a result drying rate in the sample of higher solute uptake decreased in comparison with those of lower solute uptake. For example, to obtain a moisture content = 0.25 kgH₂O/kg DM, it took 510, 1230, 810, 1350 min for fresh banana, 8h-osmosed, 10h-osmosed and 16h-osmosed samples respectively.
In addition, sugar uptake might decrease the porosity of the fruit, because it occupied the free spaces (or intercellular spaces) in fruit tissue. As a result, water transport would be inhibited, which might lead to a lower drying rate. When the foodstuff is a porous solid, for example apple, potato, porosity is one of the properties, that affects drying behavior [167]. This matter has been studied by some authors [108, 109, 114, 133, 163, 167]. Therefore, it was expected that an osmotic sample of a high sugar uptake might have lower drying rate than that of an osmotic sample with a lower level of sugar uptake.

Moreover, to verify further the role of solute uptake on drying rate, it is useful to examine osmotic dehydration using different types of sugars, which had different
levels of solute uptake. The influence of difference in uptake between sucrose and glucose osmosis on osmotic-air- dried bananas was investigated (osmotic dehydration of banana at 30°C, using 60 % syrup, immersion time: 12 hours). The results of 3 replications are summarized in Table 3.6. The results of this experiment were consistent with the previous experiments.

Table 3.6: Comparison of the effect of different solute uptake of sucrose and glucose on subsequent air-drying of osmotically pretreated bananas.

<table>
<thead>
<tr>
<th></th>
<th>Sucrose</th>
<th>Glucose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solute uptake (g/100g Fresh banana)</td>
<td>3.1 ± 0.05</td>
<td>6 ± 0.04</td>
</tr>
<tr>
<td>Equilibrium moisture content (kgH2O/kg DM)</td>
<td>0.03 ± 0.01</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>Time (min) needed for drying to moisture content 0.2 kgH2O/kg DM</td>
<td>840 ± 45</td>
<td>1350 ± 55</td>
</tr>
</tbody>
</table>

Note: Errors quoted in the table are the standard deviations of the mean for three replications.

In summary, it could be concluded that higher solute uptake in osmosed banana inhibited moisture loss during drying. This agreed well with the result of Sankat et al [45], who reported a significant decrease in drying rate for banana slabs osmosed in 39 % sucrose solution in comparison to banana osmosed in 26 % sucrose solution. The same conclusions were reported for osmotic-air dehydration of pea [106], pineapple [107, 125], grape [105], and apple [104]
3.4 CONCLUSION

Optimal osmotic conditions for banana were determined to be: 60% sucrose solution, at 30°C for 4 hours. This allowed 25 % mass loss, with minimal effects on product quality.

Variations in both temperature and concentration were shown to affect the physical characteristics of osmotic agents, which in turn had a strong impact on water transfer. Temperature had a greater effect than concentration on rate of water removal. The effect of temperature changes on water removal was marked using high sugar content syrups than low ones.

It was also shown that solute uptake by the banana is highly dependent on experimental conditions. Temperature was found to increase solute uptake at constant sugar concentration, except for some anomalies at 40°C. Only when processing at high temperature (60°C) was solute uptake linear with immersion times. Fluctuations in net solute uptake with immersion times were particularly observed at low temperature, and were most likely due to the leakage of solute from ripe banana. Thus, at 60°C, the temperature effect in accelerating solute uptake compensated for any leakage of solute from ripe banana.

Moreover, solute uptake was found to be solute dependent with glucose uptake being more than that of sucrose under the same experimental conditions. This was thought to be due to the difference of their molecular size and weight, and their physical
characteristics. Quantitative changes in solute uptake in glucose and sucrose osmosis were very dependent on experimental conditions. It could be seen that solute uptake increased to a greater extent during sucrose osmosis than for glucose osmosis at high temperature due to the possible hydrolysis of sucrose.

Besides the effect of experimental conditions, the level of solute uptake varied with maturity of fresh banana. The large changes in micro-structure during ripening of banana led to the increased leakage of solute. In addition, the increased sugar content of ripe banana, resulted in less net solute uptake in ripe banana compared to green banana.

Finally, solute uptake was found to have marked effect on subsequent air-drying rate. The higher the level of sugar uptake was, the lower the drying rate was observed. Thus, the drying rate of fresh banana was much faster than that of osmotically pretreated banana.

In general conclusion, osmotic dehydration prior to air drying showed its practical application in terms of the rate of dehydration, as well as the improvement of quality of final products such as: texture, colour, and flavour. The effect of osmotic dehydration on the quality of dried fruit has been observed by many authors [13, 62, 104, 134, 140, 141, 145]. The effect of osmotic dehydration on the improvement of banana flavour in dried products will be discussed in the next chapter.
CHAPTER FOUR

VOLATILE COMPONENTS OF FRESH AND DRIED BANANA PRODUCTS
4.1 INTRODUCTION

Bananas are nutritious fruit, have a pleasant flavor and are widely consumed throughout the world as both fresh fruit and dried products such as whole-dried bananas (banana figs) or banana chips. The flavor and aroma of the dried product are important quality factors to consider particularly with the increasing consumption of dried fruit. The major fruit flavors are volatile and they are readily lost during thermal drying. The temperature of drying will also greatly influence the physical and chemical properties of dried fruit. Moreover, new volatile flavours can be generated during processing due to the thermal decomposition of carbohydrates [168]. Both the loss of original volatile flavour components and the formation of new products are likely to play a very important role in the quality of dehydrated fruit. A better understanding of the major volatiles present in fresh as well as dried fruit, and the pathway of their formation, would provide the best solution for optimising the drying process for retaining the original “fresh-fruit” volatile flavours in the dehydrated fruit.

Banana is a typical ‘climacteric’ fruit [37] and most of its flavour constituents are only formed after maturation [169]. Esters significantly account for ‘banana-like’ and fruity aroma. The main compounds are butyl, isobutyl, and 2-pentyl acetates and butanoates [170-171]. During the ripening phase, biochemical changes result in an increase in synthesis of proteins and enzyme activities which lead to the production of flavour compounds of banana [28, 169, 172-174].
Extensive quantitative analysis of volatile banana during ripening has been carried out [31, 175, 176]. Macku and Jennings [31] studied the formation of 17 banana volatile compounds during ripening using GC analysis of dynamic headspace injections. They reported that the amounts of individual volatiles increased continuously to the onset of peel browning, after which their amounts either plateaued or decreased except in the case of ethyl acetate. The amount of this compound increased continuously up to the late senescence. The amount of total acetate esters increased significantly during ripening in comparison of the amount of total butyrate esters [31].

In general, there are three stages of banana ripening. In each stage different volatile constituents dominate the profile. Less than ripe banana, defined as green-yellow to yellow with green tips [38], shows a very simple GC profile with the “green” note from 2-hexenal, and the “green, woody, or musty notes” from methyl acetate, pentanone, butyl alcohol, amyl alcohol, hexyl alcohol [43]. These constituents are reduced or absent in the ripe banana (full yellow) [177]. Nursten [29] reported the important contribution of eugenol, o-methyleugenol and elemicin to ripe banana volatiles. There is a strong increase in levels of isoamyl and isobutyl alcohols, acetates, and butyrates in overripe banana (flecked with brown); these esters account for nearly 70% of banana volatiles.

General knowledge of the biogenesis of flavor can be of assistance in understanding the qualitative and quantitative differences of banana flavor components at different stages of maturity. Establishing of the mechanisms of production the volatile
components and characterization of their precursors is one of the ultimate goals of flavor research [172, 178].

Three main pathways for the biosynthesis of banana volatile components have been established [28, 36-38, 173]. The most important mechanism is the conversion of amino acids such as leucine, valine, isoleucine into the major esters and alcohols. The second route is the production of acids, alcohols, and esters from fatty-acid metabolism. The third route is the oxidative cleavage of linoleic and linolenic acids to C6, C9, and C12 aldehydes and oxo-acids [35].

Leucine, valine and isoleucine have been known as the source of acyl moiety in the biosynthesis of volatile banana esters [28, 33, 34, 38, 102, 172, 179]. These three compounds rapidly accumulate in banana tissue after the climacteric rise in respiration [38, 102, 172, 179] and their degradation forms ester and alcohol volatiles of banana. The degradation of valine yields methyl-branched alkyl and acyl esters, and methyl-branched alcohols [28], for example, isobutyl acetate, isobutyl alcohol. Leucine degradation yields isopentyl alcohols, and isopentyl ester [102].

The second pathway for fruit volatile formation is the conversion of fatty acids into esters, alcohols, aldehydes, or ketones. Tressl and Drawert [28] have reported in detail the transformation of octanoic acid into esters, such as caprylates and octyl esters.

The third pathway in the formation of volatile carbonyl compounds of banana is the enzymatic oxidative splitting of unsaturated fatty acids such as linolenic and linoleic
acid. Many authors [28, 173, 180-182] have studied the formation of fruit volatiles such as C6 and C9 aldehydes, and C9 and C12 oxo acids by this pathway. The particular aldehydes formed by this method depend on the maturity of banana. C9 aldehydes and oxoacids formed from linolenic acid of unripe banana [35, 183]. Whereas ripe banana synthesizes mainly C6 aldehydes, and C12 oxoacid from linoleic [35, 183]. Ripe banana treated with ethylene for 2 days at 15°C produced a mixture of these compounds, whereas banana treated with ethylene for 4 days again at 15°C only synthesized C6 aldehydes and the C12 oxoacid [183].

A considerable amount of research has been devoted to developing techniques for both qualitative and quantitative analyses of volatile components in foodstuffs. The efficiency of their separation, extraction and accurate identification are important tools for quality control for processed products. The extraction of volatile constituents from a complex matrix is a very challenging task, as the quantity and selectivity of extracted analytes are very dependent upon the extraction method utilised. Many studies have demonstrated the obvious effect of extraction method on the composition of the resultant extract [31, 168, 178, 184].

Solvent extraction, vacuum distillation and simultaneous steam distillation-extraction (SDE) are conventional methods for the extraction of fruit volatiles [27, 30, 32, 185-186] The first method is time-consuming, and has excessive solvents needs; solvent contamination in extracts is unavoidable. In addition, SDE can also cause thermal decomposition artifacts [178]. Both static and dynamic headspace sampling are widely used for volatile analysis [31, 184] as they provide volatile profiles similar to the
perceived nasal aroma [169]. However, a long sampling time, loss of extracts and possible contamination is still major problems of this technique. Due to these drawbacks, new methods of extraction have been sought, in which Solid Phase Micro-Extraction (SPME) is one of the most effective.

SPME was developed by Pawlyszyn and co-workers in 1990 [187], and it has been applied to different kinds of analytes such as air, soil, and water [188]. It has been used widely recently in analysis of foodstuffs such as caffeine in a variety of drinks [189], volatiles in drinks [184], aroma volatiles of juices and fruits [190-192], and recently Price et al. [169] applied this technique in monitoring volatile profiles of prunes during drying. Its benefits over other conventional extraction techniques are that it is solvent-free, less time-consuming and intrinsically simple. It is based on the partitioning of analytes between a coated fused silica fibre and the sample matrix. After a short equilibrium time, the absorbed analytes are thermally desorbed when the fibre is introduced into the injection port of a GC, or a GC-MS for separation and identification. It has been found that SPME is a means to simultaneous sampling, extraction, concentration, and sample introduction [193].

Drying conditions such as air temperature, air velocity and humidity, have strong effect on drying rate of foodstuff such as banana. This affects both the overall drying time, and, of course, the final quality of the dried product (for example, appearance, aroma, and taste). In order to control and minimize volatile loss in processing, optimal drying condition should be carefully chosen. Drying temperatures, and the thickness of slabs were shown in the previous chapters to strongly influence the drying rate of
banana, will be examined in this chapter to ascertain their role on the changes of volatiles during process.

Osmotic dehydration has been studied for various fruits and vegetables as the partial dehydration of fruit [194], but little information on monitoring volatile flavours of combined osmotically thermal dehydrated fruits has been reported. There are changes in membrane permeability during the ripening of climacteric fruits such as banana. These changes lead to the leakage of solute and possible volatiles as well [97, 195]. If suitable osmotic conditions are applied prior to air-drying, the retention of volatile flavors in dried banana might improve.

To completely understand the aroma of fruit, it is necessary to know the nature of the constituents present, their intensities and how the pattern of the significant constituents changes quantitatively and qualitatively during maturation and processing of the fruit. In this chapter, these aspects will be discussed with an examination of volatile profiles of fresh, osmotic-air-dried, and air-dried banana. To monitor the changes of volatile profiles, SPME in conjunction with GC and GC-MS were used for qualitative and quantitative analysis. Because of the complexity of the matrix, in this work, emphasis was laid only on those volatile constituents that are known previously to be organoleptically significant. The aim of this investigation is to not only observe what changes in volatiles occur during the drying process, but also to investigate what factors have strong effects on the loss of these components. Different drying temperatures, thickness of fruit slabs, drying times, and osmotic dehydration conditions were investigated for this purpose.
4.2 EXPERIMENTAL METHODS FOR VOLATILE ANALYSIS

4.2.1 Sample Preparation for Analysis

Analyses of volatile components were carried out on fresh and dried banana. Fifty grams of fresh banana were put in a 200 ml container. Fifty ml of saturated NaCl was added and the banana was immediately blended using a bar mixer. Saturated NaCl was used to keep all fresh banana volatile constituents in their natural proportion without being changed due to enzymatic reactions, which can occur if banana was prepared in the presence of air. The container was quickly covered by some layers of aluminum foil and capped with an airtight lid. This had a very small hole (the same size of the fibre attachment needle of SPME fibre holder). The volume ratio of headspace and aqueous phase was held constant at 1:1. The container was put in a laboratory oven (Labec, Sydney) for 40 min, at 70°C to let the sample equilibrate prior to the extraction of volatiles. Dried samples (50g) after drying under the desired conditions were prepared in a similar way to the fresh sample. Each experiment was repeated three times. The means were used to interpret the results.

4.2.2 Solid Phase Micro-Extraction Analysis

The extraction of volatile components was accomplished using a manual SPME device (Supelco, USA), consisting of a manual fibre holder (Figure 4.1) with a commercially available SPME fibre. The holder comprised a stainless steel barrel unit,
a plunger, an adjustable needle guide/depth gauge, a septum piercing needle, and a fibre attachment needle housing a 1cm length coated fused silica fibre [196].

Figure 4.1:
Schematic diagram of manual SPME device [196]

Before use, as recommended by the manufacturer, the new fibre was conditioned in the GC injector port at 250°C for 1 hour. Between uses, the fibre was kept away from contaminants in ambient air by piercing the tip of the needle into a septum of a clean
sealed vial. When sampling, the needle was inserted into the sample container through a hole in the cap. After adjusting the length of the barrel to the constant position, which was also used when injecting into the injector GC port to obtain reproducible results, the plunger was depressed to expose the fibre to the sample headspace. The fibre was then left in contact with the headspace at 40°C for 40 min (equilibrium time). Once equilibrium was reached, the fibre was withdrawn into the needle and immediately transferred to the injection port of the GC or GC-MS for analysis. Once the needle penetrated the septum of the GC port, the fibre was exposed for 2 min, and analytes were thermally desorbed onto the column. It was found necessary to run a fibre blank between some analyses. Usually, 2-min desorption was sufficient to clean the fibre.

4.2.3 Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS) analysis.

Quantification of volatiles was done by flame ionization detection (FID) using a Varian 3700 GC with a SGE BP-5 capillary column (25 m, 0.33 mm I.D., 0.25 μm film thickness). The parameters for GC system were:

- \( \text{H}_2 \) carrier gas
- Splitless injection mode
- Analytes were desorbed at 250°C for 2 min in the injection port.
- Temperature program: isothermal at 40°C for 3 min, then ramped at 4°C/min to 270°C, and held at this final temperature for 5 min.
GC data were analysed using a Shimadzu C-R 3A integrator using the following parameters: slope = 300 μV s\(^{-1}\), peak width = 4s.

The GC-MS analysis was performed with GC-17. A gas chromatograph directly interfaced to a QP-500 quadrupole mass spectrometer (Shimadzu Corporation, Japan) [168].

- Separation of the components was carried out on GC using SGE BP5 capillary column (25m length, 0.22 I.D., 0.22 mm film thickness).
- GC temperature program was isothermal at 32°C for 2 min, then raised to 250°C at the rate of 4°C/min, and held at 250°C for 2 min.
- Helium was the carrier gas run at a flow rate of 1.5 ml/min. The pressure was held at 4 kPa for 2 min, then raised at the rate of 0.6 kPa/min to 40 kPa and held for 2 min.

Other GC-MS operating parameters used are summarized in Table 4.1

Mass spectra of compounds were matched with the data found from the library of standard compounds using computerised NIST search facilities [National Institute for Standard and Technology]. The results of the identified compounds from this work using GC-MS analysis agreed with volatiles of banana reported in the literature.
Table 4.1. Gas chromatography-mass spectrometry analysis parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection temperature</td>
<td>200 °C</td>
</tr>
<tr>
<td>Desorption time</td>
<td>1 min</td>
</tr>
<tr>
<td>GC program time</td>
<td>50 min</td>
</tr>
<tr>
<td>Injection mode</td>
<td>Splitless</td>
</tr>
<tr>
<td>Scan interval</td>
<td>0.5 sec</td>
</tr>
<tr>
<td>Scan speed</td>
<td>500 amu/sec</td>
</tr>
<tr>
<td>Mass range</td>
<td>30-350 Dalton</td>
</tr>
<tr>
<td>Column pressure</td>
<td>8 kPa</td>
</tr>
<tr>
<td>Column flow</td>
<td>1.5 mL/min</td>
</tr>
</tbody>
</table>

4.3 OPTIMISATION OF SOLID PHASE MICRO-EXTRACTION

Optimization of the SPME sampling conditions is very important to obtain maximum extraction in both quantitative as well as qualitative terms. Extracting analytes from a headspace using SPME technique is an equilibrium process. Hence, analytes are not completely extracted from the matrix. In headspace SPME sampling, there are two separate processes occurring between (a) the fibre coating and the headspace, and (b) the headspace and the aqueous phase [197]. The amount of analyte absorbed on the fibre depends on the overall equilibrium between these three phases.
In headspace SPME, many factors affect the maximum extraction such as, (i) sampling time; (ii) sample volume and headspace volume; (iii) temperature of both sample equilibration and for SPME sampling; and (iv) sensitivity and selectivity of the fibre to particular analytes. The following sections will investigate the effect of the various operational parameters of the extraction process.

4.3.1 The effect of different polymer coatings

To select the most suitable fibre for extracting banana volatiles, three fibres were examined: (a) 100 µm polydimethylsiloxane (PDMS), (b) 7 µm PDMS and (c) 85 µm polyacrylate (PA). The chromatograms of banana volatiles extracted by these fibres are shown in Figure 4.2. The results of the extraction of fresh banana volatiles with these three fibres are summarized in Table 4.2.

<table>
<thead>
<tr>
<th>Fibres</th>
<th>Total peak area (µVs)</th>
<th>Number of peaks</th>
<th>Recommended for</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 µm PDMS</td>
<td>4,080,000</td>
<td>132</td>
<td>Non polar, highly volatile compounds [198]</td>
</tr>
<tr>
<td>85 µm PA</td>
<td>2,135,000</td>
<td>111</td>
<td>Non polar [198]</td>
</tr>
<tr>
<td>7 µm PDMS</td>
<td>400,000</td>
<td>82</td>
<td>Non polar, low volatile compounds [198]</td>
</tr>
</tbody>
</table>

Total peak areas are mean values of three replications given to the appropriate number of significant figures.
Figure 4.2: Banana volatile constituents extracted using three different fibre coatings.

100 μm PDMS Fibre

7 μm PDMS Fibre

85 μm PA Fibre
Moreover, to see the effect of different polymer coatings on the extraction of different volatile components, it was useful to look at a quantitative comparison of the selected peaks for various volatile compounds extracted using these three fibres. The results are illustrated in Figure 4.3.

Most of banana volatile constituents are esters, which can be semipolar, or polar compounds so both PDMS and PA fibre might be thought suitable for extracting them. However, banana volatile components differ widely in polarity as well as in volatility, so the three fibres gave different results based on their different selectivity and sensitivity to sample matrix. (i.e. the number of isolated peaks and peak intensities from GC or GC-MS chromatograms). From the results in Table 4.2, with the same sampling conditions, 100 μm PDMS fibre performed the best extraction.

Figure 4.3 Comparison of the quantitative amount of volatile banana compounds extracted using three fibres of selected peaks
Note: The combined peak areas were calculated from selected peaks having areas ≥ 10000 only.

In general, the 100 µm PDMS fibre was more effective than the 7 µm PDMS fibre, due to its thicker coating. As a result, the former could pick up greater amount of analytes. The Polyacrylate fibre gave similar results to the 100 µm PDMS fibre in the kinds of analytes extracted. However, the amount of analytes picked up by the 100 µm PDMS fibre was generally greater. This is because migration rates of analytes in and out of the PA fibre are slower due to the characteristic of its material [198].

From Figure 4.3, it can be seen that the difference between the amount of volatiles extracted from the three fibres decreased with decreased volatility of analytes. For highly volatile compounds, the difference between amount of compounds extracted with 100µm PDMS fibre and 7µm PDMS fibre was very significant, whereas, this difference was less for low volatility compounds. This meant that 7µm PDMS fibre picked up low volatility compounds more effectively than high volatile compounds and the thick coating had little affinity to low volatile compounds (high MW) [165, 197]. This agreed with the reports from many authors [165, 197, 199].

In conclusion, 100 µm PDMS fibre performed the best for extracting banana volatile components, therefore, it was used for all subsequent experiments. Other factors to enhance sensitivity for SPME technique will be discussed in the following sections.
4.3.2 Optimisation of sample equilibration and SPME sampling temperatures.

The most crucial factor for effective SPME extraction is the temperature for both sample equilibration and SPME equilibration. SPME sampling temperatures of 40°C and 60°C were examined. The results are shown in Table 4.3a.

Table 4.3a: Results of SPME sampling temperature

Note: Sample equilibrated for 40 min, at 60°C. SPME sampling time was 30 min.

<table>
<thead>
<tr>
<th>Temperature of SPME Sampling (°C)</th>
<th>Total peak area (µVs)</th>
<th>Number of peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>6,000,000</td>
<td>156</td>
</tr>
<tr>
<td>60</td>
<td>4,320,000</td>
<td>164</td>
</tr>
</tbody>
</table>

Total peak areas are mean values of three replications given to the appropriate number of significant figures.

The results of Table 4.3a showed that better extraction obtained in SPME sampling at 40°C. Sample equilibration temperatures were examined from 40°C to 80°C. The results are presented in Table 4.3b. (Note: SPME sampling was at 40 °C, for 30 min. Sample equilibrated for 40 min.)

Table 4.3b: Temperatures examined for sample equilibration

<table>
<thead>
<tr>
<th>Temperature (°C) for sample equilibration</th>
<th>Total peak area (µVs)</th>
<th>Number of peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>4,100,000</td>
<td>132</td>
</tr>
<tr>
<td>60</td>
<td>6,000,000</td>
<td>156</td>
</tr>
<tr>
<td>70</td>
<td>7,540,000</td>
<td>163</td>
</tr>
<tr>
<td>80</td>
<td>6,850,000</td>
<td>148</td>
</tr>
</tbody>
</table>
The results of Table 4.3b showed that heating the sample helped release analytes into the headspace, and facilitated extraction. However, increased temperature did not always produce positive effect on the extraction, thus when heating the sample to 80°C, the peak area and number of peaks detected decreased. There are many factors, which might be the causes of this decrease. One of which is that at high temperature the partial vapor pressure of water increased, this in turn might suppress the absorption of analytes into the fibre. In addition, high temperature (80°C) might affect the sample matrix (i.e. the depletion of some highly volatile compounds), this in turn could lead to the decrease of peak numbers and the intensity of peak areas. Therefore, 70°C was the optimal temperature for sample equilibration.

4.3.3 Optimisation of equilibration time and SPME sampling time.

The time for sample equilibration was examined over a range of 10-50 min, at a temperature of 60 °C. The results are shown in Table 4.4a

Table 4.4a: Effect of sample equilibration time

<table>
<thead>
<tr>
<th>Time for sample equilibration (min)</th>
<th>Total peak areas (μVs)</th>
<th>Number of peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>219,000</td>
<td>133</td>
</tr>
<tr>
<td>20</td>
<td>3,840,000</td>
<td>118</td>
</tr>
<tr>
<td>30</td>
<td>4,300,000</td>
<td>125</td>
</tr>
<tr>
<td>40</td>
<td>5,344,000</td>
<td>155</td>
</tr>
<tr>
<td>50</td>
<td>5,653,000</td>
<td>157</td>
</tr>
</tbody>
</table>

Total peak areas are mean values of three replications given to the appropriate number of significant figures.
From Table 4.4a it can be seen that a 40 min equilibration was sufficient to maximise the peak areas and number of peaks. There was a little increase at 50 min. Decreases in the number of peaks when using 20 and 30 minutes compared with 10 minutes may be attributed to the competition among the analytes.

Due to different volatility and affinity of analytes for the fibre coating, it was important to investigate the time for SPME sampling equilibration. SPME sampling times were examined first at the optimal condition of sample equilibration (70°C, 40 min), and the optimal temperature for SPME sampling (40°C). In addition examined results of sample equilibrated at 60°C, 40 min, and SPME sampling at 40°C were also presented to see the common trend. The results are shown in Table 4.4b

Table 4.4 b: SPME sampling time

Note: SPME sampling was at 40°C. Sample equilibrated for 40 min.

<table>
<thead>
<tr>
<th>Time for SPME equilibration (min)</th>
<th>Total peak area (µVs)</th>
<th>Number of peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample equilibrated at 70°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>7,540,000</td>
<td>163</td>
</tr>
<tr>
<td>40</td>
<td>10,460,000</td>
<td>167</td>
</tr>
<tr>
<td>50</td>
<td>6,770,000</td>
<td>152</td>
</tr>
<tr>
<td>60</td>
<td>8,860,000</td>
<td>149</td>
</tr>
<tr>
<td>Sample equilibrated at 60°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>5,340,000</td>
<td>155</td>
</tr>
<tr>
<td>30</td>
<td>6,000,000</td>
<td>156</td>
</tr>
<tr>
<td>40</td>
<td>3,890,000</td>
<td>188</td>
</tr>
<tr>
<td>50</td>
<td>6,710,000</td>
<td>171</td>
</tr>
</tbody>
</table>
Total peak areas are mean values of three replications given to the appropriate number of significant figures.

It can be seen that at the optimal conditions for sample equilibration (70°C, 40 min) and SPME equilibration (40°C), 40 min was sufficient for most volatile compounds to be extracted. After 50 min, a drop in peak area and number of peaks was observed. When the sample was equilibrated at 60°C, this drop was observed between 30 and 40 min. Subsequently, the amount of analyte extracted increased again in these both cases examined above. This is a well-known fact [197]. It is thought to be caused by the non-equilibrium situation, in which the diffusion of analytes into the polymer coatings dominates the overall process due to the steep concentration gradient in operation [197]. The concentration gradient might be different at different times of SPME sampling due to the gap between sample equilibration temperature and SPME sampling temperature. In brief, due to the convenience of the routine analyses, 40 min for SPME sampling was considered the best, although at this time all analytes might not reach equilibration, due to differences of their partition.

In summary, the optimal conditions for extraction of banana volatiles using 100µm PDMS fibre were sample equilibrated at 70°C, for 40 min, and SPME sampling equilibrated at 40°C, for 40 min.
4.3.4 Evaluation of SPME Technique for the Extraction of Banana Volatiles.

The reproducibility of the SPME technique was examined using blended fresh banana, and the results are summarized in Table 4.5.

Table 4.5:

Reproducibility of Headspace SPME Technique Using 100μm PDMS Fibre for the Extraction of Selected Volatile Compounds from Fresh Blended Banana (using optimal sampling conditions, for three replications).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Retention Time (min)</th>
<th>% RSD of Retention time</th>
<th>Relative concentration (%)</th>
<th>% RSD of Relative Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylpropyl acetate</td>
<td>3.5</td>
<td>0.6</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Hexanal</td>
<td>4</td>
<td>1.1</td>
<td>5.3</td>
<td>3.6</td>
</tr>
<tr>
<td>n-Butyl acetate</td>
<td>4.35</td>
<td>1.01</td>
<td>2.3</td>
<td>8.95</td>
</tr>
<tr>
<td>2-Hexenal</td>
<td>5.35</td>
<td>0.94</td>
<td>7.2</td>
<td>9.8</td>
</tr>
<tr>
<td>Isopentyl acetate</td>
<td>6.1</td>
<td>0.4</td>
<td>19.7</td>
<td>4</td>
</tr>
<tr>
<td>Isobutyl butanoate</td>
<td>8.7</td>
<td>0.13</td>
<td>2.9</td>
<td>1.6</td>
</tr>
<tr>
<td>2-Methyl 1-pentanol</td>
<td>10.8</td>
<td>0.68</td>
<td>0.9</td>
<td>12.5</td>
</tr>
<tr>
<td>Pentyl butanoate</td>
<td>11.2</td>
<td>0.73</td>
<td>3.1</td>
<td>2.3</td>
</tr>
<tr>
<td>5-hexen-2-one</td>
<td>11.8</td>
<td>0.84</td>
<td>4.1</td>
<td>4.3</td>
</tr>
<tr>
<td>3-methylbutyl isobutanoate</td>
<td>12.5</td>
<td>0.73</td>
<td>13.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Isoamyl isovalerate</td>
<td>14.3</td>
<td>0.69</td>
<td>6.1</td>
<td>3.9</td>
</tr>
</tbody>
</table>
The results showed that the techniques had an excellent reproducibility for different samples (i.e. experiments were repeated from bananas harvest at different times of the year). Three replicates of measurements were performed using the same extraction conditions. Most relative standard deviations (% RSD) for retention times of major volatile compounds were less than 1% except for two peaks (Rt = 4 and 4.35). Variations in relative concentrations for the 11 peaks studied were from 0.59% to 12.5%, of which 8 values were less than 5%. These results indicated that this technique is reliable for quantitative as well as qualitative analysis of most volatiles in fruit.

4.4 VOLATILE CONSTITUENTS OF FRESH BANANA

The GC-MS profile of fresh ripe banana volatiles extracted using a 100 μM Polydimethylsiloxane-Coated SPME fibre, is shown in Figure 4.4. Table 4.6 identified the banana volatile constituents in this profile.

From this work, 52 volatile components of banana were positively identified. Most of these compounds had been previous reported in the literature, (where conventional headspace analysis had been used). Esters comprised the largest group of volatile components of banana. From this work, 50% of banana volatile constituents were esters, of which acetates and butyrates predominate. McCarthy et al. [200] assigned the banana-like components to amyl esters and the fruity ones to butyl esters [35], whereas alcohols and carbonyls give odours described as green, woody, or musty.
Figure 4.4: GC-MS Chromatogram of the Headspace Flavour Constituents of Fresh Blended Banana Extracted Using 100μm Polydimethylsiloxane-Coated SPME Fibre
Table 4.6: List of Volatile Constituents of Fresh Banana identified by GC-MS from SPME Extraction of Blended banana.

(Note: The orders of peaks in this table were the numbers of peaks in Figure 4.4, major volatiles were bold).

<table>
<thead>
<tr>
<th>Peak order</th>
<th>Retention time</th>
<th>COMPOUNDS</th>
<th>In literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.13</td>
<td>Acetaldehyde</td>
<td>✓</td>
</tr>
<tr>
<td>2</td>
<td>1.233</td>
<td>Ethanol</td>
<td>✓</td>
</tr>
<tr>
<td>3</td>
<td>1.661</td>
<td>Ethyl acetate</td>
<td>✓</td>
</tr>
<tr>
<td>4</td>
<td>2.201</td>
<td>2-Pentanone</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>2.350</td>
<td>2-Pentanol</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>2.509</td>
<td>n-Propyl acetate</td>
<td>✓</td>
</tr>
<tr>
<td>5</td>
<td>2.838</td>
<td>1-Pentanol</td>
<td>✓</td>
</tr>
<tr>
<td>6</td>
<td>3.474</td>
<td>2-Methylpropyl acetate</td>
<td>✓</td>
</tr>
<tr>
<td>7</td>
<td>3.997</td>
<td>Hexanal</td>
<td>✓</td>
</tr>
<tr>
<td>8</td>
<td>4.346</td>
<td>n-Butyl acetate</td>
<td>✓</td>
</tr>
<tr>
<td>9</td>
<td>5.224</td>
<td>1-Methylbutyl acetate</td>
<td>✓</td>
</tr>
<tr>
<td>10</td>
<td>5.35</td>
<td>2-Hexenal</td>
<td>✓</td>
</tr>
<tr>
<td>11</td>
<td>6.1</td>
<td>Isopentyl acetate</td>
<td>✓</td>
</tr>
<tr>
<td>12</td>
<td>6.432</td>
<td>2-Heptanone</td>
<td>✓</td>
</tr>
<tr>
<td>13</td>
<td>6.55</td>
<td>4-Hepten-2-one</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>7.246</td>
<td>Isobutyl isobutanoate</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>8.248</td>
<td>4-Methyl-2-pentyl acetate</td>
<td>✓</td>
</tr>
<tr>
<td>14</td>
<td>8.711</td>
<td>Isobutyl butanoate</td>
<td>✓</td>
</tr>
<tr>
<td>Peak order</td>
<td>Retention time</td>
<td>COMPOUNDS</td>
<td>In literature</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td>----------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>15</td>
<td>10.176</td>
<td><strong>Butyl butanoate</strong></td>
<td>✔</td>
</tr>
<tr>
<td>•</td>
<td>10.543</td>
<td>Not identified</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>10.787</td>
<td><strong>2-Methyl 1-pentanol</strong></td>
<td>✔</td>
</tr>
<tr>
<td>17</td>
<td>11.194</td>
<td><strong>Pentyl butanoate</strong></td>
<td>✔</td>
</tr>
<tr>
<td>•</td>
<td>11.499</td>
<td>3-Heptenyl acetate</td>
<td>✔</td>
</tr>
<tr>
<td>18</td>
<td>11.79</td>
<td>5-hexen-2-one</td>
<td>Not found</td>
</tr>
<tr>
<td>•</td>
<td>12.043</td>
<td>Butyl isovalerate</td>
<td>✔</td>
</tr>
<tr>
<td>19</td>
<td>12.479</td>
<td><strong>3-methylbutyl isobutanoate</strong></td>
<td>✔</td>
</tr>
<tr>
<td>20</td>
<td>14.039</td>
<td>2-methylbutyl 2-methyl butanoate</td>
<td>✔</td>
</tr>
<tr>
<td>21</td>
<td>14.299</td>
<td><strong>Isoamyl isovalerate</strong></td>
<td>✔</td>
</tr>
<tr>
<td>22</td>
<td>16.041</td>
<td>trans 2-Hepten-1-ol</td>
<td>✔</td>
</tr>
<tr>
<td>23</td>
<td>17.346</td>
<td>Not identified</td>
<td>✔</td>
</tr>
<tr>
<td>24</td>
<td>17.44</td>
<td>Hexyl butanoate</td>
<td>✔</td>
</tr>
<tr>
<td>25</td>
<td>17.599</td>
<td>3-Octenyl acetate</td>
<td>✔</td>
</tr>
<tr>
<td>26</td>
<td>17.979</td>
<td>3-Hexenyl acetate</td>
<td>✔</td>
</tr>
<tr>
<td>27</td>
<td>18.168</td>
<td>2, 4-Dimethylcyclo pentanol</td>
<td>Not found</td>
</tr>
<tr>
<td>28</td>
<td>19.242</td>
<td><strong>Isobutyl isovalerate</strong></td>
<td>✔</td>
</tr>
<tr>
<td>29</td>
<td>19.541</td>
<td>Unresolved mixture of compounds of peak 29, 30</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>19.635</td>
<td>Not identified</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>23.605</td>
<td>1,3-cyclooctadiene</td>
<td>Not found</td>
</tr>
<tr>
<td>Peak order</td>
<td>Retention time (min)</td>
<td>COMPOUNDS</td>
<td>In literature</td>
</tr>
<tr>
<td>-----------</td>
<td>---------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>32</td>
<td>23.84</td>
<td>Butanoic acid, 1-ethenylhexyl ester</td>
<td>✓</td>
</tr>
<tr>
<td>33</td>
<td>24.214</td>
<td>cis-Cyclodecene</td>
<td>Not found</td>
</tr>
<tr>
<td>34</td>
<td>24.346</td>
<td>3-Decene-1-yne</td>
<td>Not found</td>
</tr>
<tr>
<td>35</td>
<td>25.242</td>
<td>Not identified</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>25.48</td>
<td>2-octen-1-ol</td>
<td>✓</td>
</tr>
<tr>
<td>37</td>
<td>25.652</td>
<td>Mixture of isomeric octenols</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>25.845</td>
<td>Cis-3-Hexenyl 2-methylbutanoate</td>
<td>✓</td>
</tr>
<tr>
<td>39</td>
<td>29.32</td>
<td>Benzene 1,2,3-trimethoxy-5-(2-propenyl)-(i.e. <strong>Elemicin</strong>)</td>
<td>✓</td>
</tr>
<tr>
<td>40</td>
<td>29.85</td>
<td>3-Decen-1-ol</td>
<td>Not found</td>
</tr>
<tr>
<td>41</td>
<td>30.712</td>
<td>Phenol, 2,6-dimethoxy-4-(2-propenyl)-</td>
<td>✓</td>
</tr>
<tr>
<td>42</td>
<td>31.433</td>
<td>Not identified</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>37.346</td>
<td><strong>Isopropyl myristate</strong></td>
<td>✓</td>
</tr>
<tr>
<td>*</td>
<td>38.723</td>
<td>6-Undecylamine</td>
<td>Not found</td>
</tr>
<tr>
<td>44</td>
<td>42.343</td>
<td>Propyl hexadecanoate</td>
<td>✓</td>
</tr>
</tbody>
</table>

Most previous work on the extraction of banana volatile compounds was carried out by steam or vacuum distillation [30, 38], and static or dynamic headspace [29, 178] from sliced or blended banana. GC in conjunction with GC-MS was then used to
separate and identify the volatile components. The volatile profiles from these studies [26, 30, 32, 185, 200, 201] showed much similarity with the present results. However, the SPME technique is simple and more sensitive. For example, Wick et al [172] used more than 10 kg banana in the distillation of banana volatiles.

Volatile constituents of banana are not evenly distributed within fruit [202]. Perhaps the reason for this fact is that amino acids such as leucine, valine, isoleucine, which are the precursors of banana volatiles, are not evenly distributed within green banana [202]. They are concentrated in the center region of slab (the placenta) than that of in the surrounding region (the pericap). The diagram of these two portions is shown below.

As a result of this, when bananas are ripe, volatiles formed from these precursors, will be unevenly distributed within fruit. It is interesting to confirm this fact by looking at the volatile profiles of two portions of banana slabs, say the pericap and the placenta. This is shown in Table 4.7, where only the results for major compounds were
The data was expressed as the ratio of peak area of compounds in the center portion (placenta) over those of in the surrounding portion (pericap). In general, the amount of volatile compounds in placenta was nearly double that in the pericap. Some compounds were significantly unevenly distributed in the two regions, for example 2-methylpropyl acetate, and isoamyl isovalerate. This fact might affect the loss of these compounds during processing. This matter will be discussed later.

Table 4.7: The differences between the contents of 10 major volatile constituents in two portions of banana slabs.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Retention time (min)</th>
<th>Ratio peak area of compounds in the placenta: peak area in pericap.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylpropyl acetate</td>
<td>3.47</td>
<td>180</td>
</tr>
<tr>
<td>Hexanal</td>
<td>3.99</td>
<td>0.6</td>
</tr>
<tr>
<td>2-hexenal</td>
<td>5.35</td>
<td>0.72</td>
</tr>
<tr>
<td>Isopentyl acetate</td>
<td>6.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Isobutyl butanoate</td>
<td>8.7</td>
<td>1.6</td>
</tr>
<tr>
<td>5-Hexen-2 one</td>
<td>11.8</td>
<td>1.16</td>
</tr>
<tr>
<td>3-Methylbutyl isobutanoate</td>
<td>12.48</td>
<td>1.5</td>
</tr>
<tr>
<td>Isoamyl isovalerate</td>
<td>14.30</td>
<td>8.9</td>
</tr>
<tr>
<td>3-Octenyl acetate</td>
<td>17.6</td>
<td>1.37</td>
</tr>
<tr>
<td>Elemicin</td>
<td>29.3</td>
<td>0.9</td>
</tr>
<tr>
<td>Ratio of total peak areas of all compounds in the placenta/ that in the pericap.</td>
<td></td>
<td><strong>1.8</strong></td>
</tr>
</tbody>
</table>

(In all cases, the standard deviations in the mean ratios were in the range of 1- 4% for 3 replications)
4.5 CHANGES OF BANANA VOLATILE CONSTITUENTS DURING AIR-DRYING

Changes during drying were examined at different temperatures (at the same % mass loss). The aim of these experiments was to investigate two things: i) the influence of drying temperature on possible thermal degradation of banana volatiles in the dried product. ii) The influence of drying rate on the loss of volatiles. In addition, changes in the volatile profile were also examined for various drying times at the same temperature. These experiments were carried out to ascertain the extent of loss of some major banana volatiles during drying.

4.5.1 Qualitative Changes of Volatiles during Air-Drying of Fresh Banana at Different Temperatures

Drying was carried out at 60°C (28 hours), 70°C (20 hours), 80°C (16 hours), 90°C (12 hours), and 100°C (10 hours). The percentage mass loss from these experiments was about 74%. No new peaks were found in any of the volatile profiles of banana under these drying conditions. Only changes in relative proportions of volatile constituents were found. This was illustrated in Figure 4.5 with 3 chromatograms of fresh banana and banana dried at 90°C and 100°C to 74 % mass loss.
Figure 4.5: GC-MS chromatograms of the headspace flavour constituents of (a) fresh, (b) dried banana at 90 °C, and (c) dried banana at 100 °C extracted using 100 µm polydimethylsiloxane-coated SPME fibre.
The fact that no new peaks were found in dried banana under these various drying conditions raised some interesting questions.

Reactions such as Maillard and caramelisation often occur in drying fruit. These reactions, which cause changes in volatiles of dried fruit, have been reported in the literature [203, 204, 169]. Maillard reaction occurs between reducing sugars and amino acids in fruit. This reaction proceeds effectively at temperature greater than 50 °C, and at pH 4-7 [123, 204]. The pH of ripe banana was about five, and the drying temperatures used were favorable for Maillard reaction. However, there was no evidence of this chemical degradation reaction occurring during drying from the changes in the SPME profiles. This could be due to the fact that the amount of reducing sugar (i.e. glucose) in ripe banana was much less than the amount of sucrose [19, 162], and that some amino acids were precursors of banana volatiles. These compounds were converted to volatiles (most of them are esters) as the banana ripened. Therefore, the significantly decreased amount of these amino acids in ripe banana compared to other fruit might possibly lead to there being no significant Maillard activity in drying banana. Esters do not usually undergo this reaction.

Caramelisation occurs between sugars and carbonyl compounds [204] in the absence of amino acids. This reaction requires high temperature (>120°C), 9 <pH< 3 [204], and the surface of fruit is strongly heated to a very low moisture content. High drying temperature (>100°C) is not favored for high quality dried banana, because of the production of a brown color and off-flavor [45]. At experimental temperatures used here, volatile compounds of banana did not undergo caramelisation.
The little difference in volatile profiles between dried bananas at these conditions and the fresh banana was consistent with the report of Uzelac et al [39]. However, Hultin and Proctor [30] reported that in heat-processed pureed banana, 2 unidentified volatile constituents found which were not in their fresh banana samples.

Drying at a very high temperature (>100°C) gave a bad appearance to the final product. Therefore, 80°C was the highest temperature used to investigate the effect of drying conditions on the changes to banana volatiles in the following sections. Moreover, due to there being little evidence of new compounds in the volatile profiles of dried banana, the following investigations will focus only on the quantitative changes of volatile constituents with drying conditions.

4.5.2 The effect of temperature and drying rate on the loss of banana volatiles during drying.

To investigate the influence of temperature on the changes of volatiles during the drying process, fresh bananas were dried at different temperatures (60, 70, and 80°C). Drying times for these experiments were set up to obtain the same percentage mass loss of all samples. The banana was dried to 60% mass loss at 60°C (8 h), 70°C (6h) and 80°C (4h). The results are presented in Table 4.8. Data was expressed as the ratio of the peak area of the constituents in the fresh banana sample over the peak area of the same in dried banana. Since many volatile constituents of fresh banana were identified in this work, to simplify the investigation, only selected major constituents were discussed in this section.
The peak area ratio gave a semi quantitative indication of the amount of a volatile which was lost during processing. It was used throughout the rest of this chapter. Besides the ratios of selected peaks presented, the ratios of total peak area of fresh sample / total peak area of examined samples (i.e. all peaks of the chromatogram) were also presented to see the general trend and the consistency to other data of selected peaks.

From the results in Table 4.8, it can be seen that at the same level of mass loss, drying at 70°C led to a faster depletion of banana volatiles than at other temperatures. For some volatile compounds, the difference between the values of drying at 70°C and at other temperatures was very considerable (P < 0.05 in all significance tests).

At 60 % mass loss, in general, the level of volatile loss of drying at 80°C was generally less than that of at 60°C. However, the differences between these two drying temperatures were not very significant in comparison with 70°C. The reason for this temperature dependent retention of volatiles might be the influence of the drying rate. This matter will be discussed in the next section.

To observe the influence of drying rate (especially the initial drying rate) on the changes to volatiles, fresh bananas were dried to a low moisture content (i.e. around 70 %ML) at 70°C (12h) and 80°C (6h). The results are also presented in Table 4.8 for case of 70% mass loss. Drying at 80°C helped to prevent significant loss of volatiles in comparison with drying at 70°C, because of the significantly reduced drying time.
Table 4.8: Comparison of the semi-quantitative changes for major banana volatiles in banana slabs dried to 60 % and 70 % mass loss at various temperatures.

<table>
<thead>
<tr>
<th>Rt (min)</th>
<th>Compounds</th>
<th>60% Mass Loss</th>
<th>70% Mass Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>60°C, 8h</td>
<td>70°C, 6h</td>
</tr>
<tr>
<td>5.35</td>
<td>2-Hexenal</td>
<td>21.7</td>
<td>141</td>
</tr>
<tr>
<td>6.1</td>
<td>Isopentyl acetate</td>
<td>40.2</td>
<td>167</td>
</tr>
<tr>
<td>8.7</td>
<td>Isobutyl butanoate</td>
<td>7.3</td>
<td>38.4</td>
</tr>
<tr>
<td>10.2</td>
<td>Butyl butanoate</td>
<td>4.7</td>
<td>13</td>
</tr>
<tr>
<td>10.8</td>
<td>2-Methyl 1-pentanol</td>
<td>13.8</td>
<td>60.6</td>
</tr>
<tr>
<td>11.2</td>
<td>Pentyl butanoate</td>
<td>1.5</td>
<td>4.4</td>
</tr>
<tr>
<td>11.8</td>
<td>5-hexen-2-one</td>
<td>5.5</td>
<td>9.6</td>
</tr>
<tr>
<td>12.5</td>
<td>3-methylbutyl isobutanoate</td>
<td>2.4</td>
<td>6.2</td>
</tr>
<tr>
<td>14.3</td>
<td>Isoamyl isovalerate</td>
<td>1.5</td>
<td>3.2</td>
</tr>
<tr>
<td>17.6</td>
<td>3-octenyl acetate</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>29.32</td>
<td>Elemicin</td>
<td>2.4</td>
<td>2.9</td>
</tr>
<tr>
<td>37.35</td>
<td>Isopropyl myristate.</td>
<td>0.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Ratio of TOTAL peak area of fresh sample / total peak area of examined samples</td>
<td>6.7</td>
<td>11.7</td>
<td>3.9</td>
</tr>
</tbody>
</table>

(In all cases, the standard deviations in the mean ratios were in the range of 1-4% for 3 replications)

There were two reasons why drying at a high initial rate favors the retention of banana volatiles. The first reason was that drying at high initial rate resulted in the rapid
formation of a hard layer on the surface of the slabs. This layer might hinder the evaporation of both water as well as volatiles. In addition, according to selective diffusion theory [205], volatiles were lost in the early stage of drying. At this stage, moisture content is high in fruit, and water evaporates together with volatiles. When moisture content fell below a certain level, water continued to be lost, but the diffusivity of volatile components dropped dramatically and the removal of these substances fell close to zero. That was the reason why the initial drying rate was important to the extent loss of volatiles. The faster the initial drying rate was the less loss of volatiles resulted. This was understandable, since the temperature in the fruit at this stage was still lower than the drying temperature, so the effect of temperature was less on the loss of volatiles or on reactions, which could occur and affect the fruit components.

On the other hand, shortening of the total drying rate will also help reduce the loss of volatile compounds, by reducing of the length in contact to high temperature. The results for 70 % mass loss illustrated this trend clearly. It took double the drying time at 70°C (12h) to get the same mass loss as drying at 80°C (6h). Significant loss (P<0.05) for highly volatile compounds occurred even when drying to 60 % mass loss, at 70°C (6h). Therefore, if the time were prolonged, greater loss would be expected.

An interesting fact from the results in Table 4.8 was the effect of various drying conditions on the changes of volatiles was stronger for highly volatile compounds
(Rt < 14.3 min) than for less volatile compounds (Rt > 14.3 min). This might be partly explained by their low volatility, and higher molecular weight (hence lower D), so their loss at the beginning of drying (i.e. the influence of initial drying rate) was small.

In summary, both temperature and initial drying rate had considerable effect on the loss of volatile components during the drying process. The initial drying rate had a stronger effect than the temperature on the maintenance of volatile compound of dried banana.

In addition to the effect of drying conditions on the overall extent volatile loss, it was interesting to investigate the extent of this loss at various drying times at a constant temperature.

4.5.3 The Effect of Drying Time on Changes in Volatile Constituents

Fresh bananas were dried at 60°C for 4 h, 8 h, 10 h, 12 h, and 28 h. Quantitative changes of banana volatile compounds were found to depend on the volatility of the components and their spatial distribution in the slabs. The results are summarized in Table 4.9 and show the extent of loss for major compounds.

To see clearly the different trends for high and low volatility compounds, the results were presented in two groups. The first group was for major constituents with retention times smaller than 14.3 min (highly volatile compounds) and the second group for compounds with retention times between 14.7 and 37.35 min (less volatile
compounds). A comparison of the changes in the volatile constituents of different locations in slabs was also given.

Table 4.9: Summary of the semi-quantitative changes of some major banana volatile constituents during drying at 60°C (refer to table 4.7 for the distribution of volatile compounds in slabs)

<table>
<thead>
<tr>
<th>Drying time (hours)</th>
<th>Compounds having Rt &lt;14.3 min</th>
<th>Compounds having Rt ≥ 14.3 min</th>
<th>Compounds of high content in the placenta</th>
<th>Compounds of high content in the pericap</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>1</td>
<td>1.8</td>
<td>1.3</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>1</td>
<td>3.3</td>
<td>1.7</td>
</tr>
<tr>
<td>10</td>
<td>10.2</td>
<td>1</td>
<td>4.7</td>
<td>1.7</td>
</tr>
<tr>
<td>12</td>
<td>14.2</td>
<td>1.1</td>
<td>3.7</td>
<td>1.9</td>
</tr>
<tr>
<td>28</td>
<td>37</td>
<td>1.6</td>
<td>6.7</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Note: Compound A = 2-Methylpropyl acetate (Rt = 3.47 min)

Compound B = Isoamyl isovalerate (Rt = 14.3 min)

Compound C = 2-Hexanal (Rt = 5.35 min)

In all cases, the standard deviations in the mean ratios were in the range of 1-5% for 3 replications.
From this table, it can be seen clearly that during drying, the loss of compounds was dependent on their volatility. In general, the highly volatile compounds were lost more significantly than the less volatile compounds under the same drying conditions (temperature, and time). The different levels of volatile loss between two groups were found to increase with drying time. After drying for 4 hours, the loss of highly volatile compounds was five times more than that of the less volatile compounds. After drying for 28 hours, the loss of highly volatile group was over 20 times more than that of the less volatile group.

From Table 4.9, it was seen that the loss of 2-Hexenal (Rt=5.35 min) was significantly faster (P<0.05) than that of 2-Methylpropyl acetate (Rt=3.47 min) and isoamyl isovalerate (Rt = 14.3 min). There is little difference in boiling points between 2-Methylpropyl acetate and 2-Hexenal. (The values are 126°C and 131°C respectively) [206]. Therefore, volatility may not be helpful to explain this difference. It is known that volatile constituents of banana are not evenly distributed within fruit [203] (referring to section 4.4 and table 4.7 for this information). Thus, it might be expected that the constituents with higher contents in the surrounding region would be lost more easily during drying, especially at high drying temperature. For example, 2-Hexenal (Rt=5.35) lost significantly (P<0.05) than two other compounds after drying only 4 hours, and after drying for 10h, 2-Hexenal had almost completely disappeared. In contrast, the amount of 2-Methylpropyl acetate (Rt=3.46) changed very slowly during drying 28 hours. From table 4.7 it was seen that 2-Methylpropyl acetate was present only in the central region of banana slab. Due to this natural distribution of its content, it was protected, and the result was its loss during drying was much lower. A similar
trend was seen for isoamyl isovalerate (Rt =14.32). Isoamyl isovalerate is also lower volatility than 2-Methylpropyl acetate. This explained its better retention during drying than that for 2-Methylpropyl acetate.

In summary, both volatility and distribution of the components control the level of loss during drying. Another important factor was likely to be the thickness of the banana slice. Thickness of the fruit will have a major influence on the drying rate. This will be investigated in the next section.

4.5.4 The Influence of Thickness of Banana Slabs on the Retention of Volatiles during Air-Drying

To confirm the important role of drying rate on the loss of volatile components, the drying of banana slabs of different thickness at a constant temperature was investigated.

Experiments were carried out at 60°C and 80°C with banana samples of 2 cm, 1 cm and 0.2 cm thickness. All samples were dried to the same percentage ML (around 71 % ML). The corresponding drying times at 80°C were 5 h, 7 h and 10 h for 0.2 cm, 1 cm, and 2 cm banana slabs respectively. Whilst at 60°C, the drying times were 10 h, 16 h and 22 h. The results of these experiments are presented in Table 4.10.
Table 4.10: Effect of slab thickness on the volatile loss of banana dried at 60 °C and 80 °C.

<table>
<thead>
<tr>
<th>Drying temperature (°C)</th>
<th>60</th>
<th></th>
<th>80</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of slabs (cm)</td>
<td>0.2</td>
<td>1</td>
<td>2</td>
<td>0.2</td>
</tr>
<tr>
<td>Ratio of Peak Area of Fresh sample/Peak Area of examined samples</td>
<td>5.1</td>
<td>3.7</td>
<td>6.3</td>
<td>3.7</td>
</tr>
</tbody>
</table>

In all cases, the standard deviations in mean ratios were between 2-3% for 3 replications.

In general, for the all thickness tested, the loss of volatiles was least if drying at 80°C in keeping with the results from previous sections. 1 cm slabs lost least amount of volatiles at both temperatures, whilst 2 cm slabs lost the most. The difference in volatile loss between 0.2 cm and 2 cm was not though very significant.

At the same temperature, 0.2 cm slabs would be affected by thermal heat more than the thicker slabs. At the beginning of drying, this was due to the difference between the temperatures of the surface and the center of fruit being less in thin slabs. Therefore, volatiles in the center region of fruit would be more quickly lost. By contrast, 2 cm slabs had a lower initial drying rate, resulting in a longer drying time. This in turn meant that volatile compounds were in contact with heat for a longer drying time, and thus greater loss of volatile resulted.

In conclusion, a high initial drying rate favored the retention of volatiles. Therefore, banana should be dried at a high temperature at this stage. One-cm slabs were found to
be suitable for drying at high temperature to obtain that high drying rate, with optimal retention of volatile compounds.

### 4.6 CHANGES OF VOLATILE COMPONENTS OF OSMOTIC-AIR-DRIED BANANA

Osmotic dehydration of ripe banana slabs prior to air-drying was performed under different osmotic conditions. The variables looked at were: nature of sugar and the duration of the osmotic process. In addition, thermal osmotic dehydration of green banana was carried out to compare with the results with ripe samples. The aim of these experiments was to confirm the role of osmotic dehydration on retaining volatiles of dried banana and to find the optimal osmotic conditions prior to air-drying to reduce the loss of volatile compounds.

Moreover, in the light of previous work it was interesting to examine whether a short period of air-drying at high temperature, prior to osmotic dehydration, could retain volatile components better than osmotic dehydration alone.

In addition, headspace SPME analysis of sucrose syrup used in osmotic dehydration of green and ripe banana was carried out to compare the different levels of volatile loss during osmotic dehydration between these samples. The sampling conditions for
headspace SPME of these syrups were similar to that for banana samples. All examined samples under the range of conditions are given as followings:

Note: All osmotically dehydrated samples were carried out at 30°C, 60% sugar solution. They were subsequently air-dried to constant weight.

<table>
<thead>
<tr>
<th>Name of Samples</th>
<th>Fresh banana (Green and ripe)</th>
<th>Air-drying of Fresh Banana (Green and ripe)</th>
<th>Osmotic Air-dried banana (Ripe and Green *)</th>
<th>Sucrose solution used in osmotic dehydration of green and ripe banana</th>
<th>Multi-step dehydration of ripe banana</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of samples</td>
<td>2</td>
<td>2</td>
<td>7</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Experimental conditions</td>
<td>28 h, 60°C</td>
<td>Sucrose, Glucose osmosis</td>
<td>Immersion time: 6 h</td>
<td>Air-drying at 80°C (2 h), or 60°C (4 h) then</td>
<td>Multi-step dehydration of ripe banana</td>
</tr>
<tr>
<td></td>
<td>• Immersion time:</td>
<td>• Osmotic dehydration</td>
<td>• Osmotic dehydration with sucrose solution for 6 h.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2, 6, 12 h</td>
<td>• Subsequent air-drying for 30 h, at 60°C</td>
<td>• Subsequent air-drying for 30 h, 60°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Note:** This sample was carried out only for sucrose osmosis 6 h.
In order to see the general trends, the results of this section did not focus on the quantitative changes of individual major peaks, but total peak areas of all volatile components. This was used to compare the effect of different osmotic conditions on the retention of volatile components in dried banana. As before, all the results were expressed as the ratios of total peak areas of fresh samples over total peak areas of dehydrated samples.

4.6.1 The effect of osmotic dehydration on retention of volatiles.

Osmotic dehydration prior to air-drying improved the maintenance of volatile compounds of dried banana. This is illustrated in Figure 4.6, which shows the results of two GC chromatograms of osmotic-air-dried sample, and air-dried sample. The former sample was osmosed with 60% solution glucose, at 30°C, for 12 h prior to air-drying at 60°C to a constant weight for 30 hours. This sample was left over 8 months before the experiment was carried out. From this figure, it can be seen that the retention of volatiles was better in osmotically pretreated sample compared with the sample without osmotic dehydration prior to air-drying.

4.6.2 Effect of banana maturity on the volatile loss during osmotic dehydration

The more open structure of ripe banana tissue was likely to be the main reason for the large volatile loss in osmotic dehydration of ripe banana. This loss was found to be more in ripe banana than for in green banana. This was because of volatile loss in osmotic agents during processing (i.e. analysis of the headspace of syrup used in
osmotic dehydration of green and ripe banana). Another experiment was carried out to compare the retention of volatile compounds in green and ripe banana after these samples were osmosed and then air-dried. In addition, to confirm further the role of the open structure in different volatile loss in green and ripe banana, a comparison of the retention of volatiles in air-drying of green and ripe banana was also investigated.

Figure 4.6: Comparison of GC chromatograms of air-dried banana (at 60°C, for 28 hours), and of osmotic-air-dried banana stored for 8 months.
The presence of all major volatile components in headspace of sucrose solution used in osmotic dehydration of ripe banana was shown in Figure 4.7. The changes in volatile compounds from ripe and green bananas subjected to osmotic-air-dehydration are presented in Table 4.11. The results were expressed in terms of the ratios of total peak areas of fresh (green or ripe) samples over total peak areas of the corresponding dehydrated samples.

From the chromatograms in Figure 4.7, it can be seen that major volatiles partitioned to a similar extent between fresh, osmotically dried banana and the sugar solution after osmotic dehydration. This was not surprising, as fresh banana consists of a high level of H₂O and high sugar as in the other samples [93]. Moreover, most of the major volatile constituents were found to be lost during osmotic processing.

Table 4.11: The comparison of volatile loss in green and ripe banana during osmotic dehydration and subsequent air-drying.

<table>
<thead>
<tr>
<th>Examined Samples</th>
<th>The Ratio of total peak area of fresh banana / total peak area of examined sample.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-drying samples of</td>
<td></td>
</tr>
<tr>
<td>(1) Ripe fresh banana</td>
<td>15.2*</td>
</tr>
<tr>
<td>(2) Green fresh banana</td>
<td>2.3 **</td>
</tr>
<tr>
<td>Osmotic-air-dried samples of</td>
<td></td>
</tr>
<tr>
<td>(3) Ripe banana (sucrose 6h)</td>
<td>3.5 *</td>
</tr>
<tr>
<td>(4) Green banana (sucrose, 6h)</td>
<td>1.7 **</td>
</tr>
<tr>
<td>Syrup (sucrose, 6h osmosis) used in</td>
<td></td>
</tr>
<tr>
<td>(5) Osmotic dehydration of green banana</td>
<td>3</td>
</tr>
<tr>
<td>(6) Osmotic dehydration of ripe banana</td>
<td>1.7</td>
</tr>
</tbody>
</table>
In all cases, the standard deviations in the mean ratios were between 2-3% for 3 replications.

Note: * The ratio of peak area of ripe fresh banana / peak area of examined sample of ripe banana.

** The ratio of peak area of green fresh banana / peak area of examined sample of green banana.

From the results in Table 4.11 it can be seen that after osmotic dehydration and then air-drying, the loss of volatile compounds in ripe banana was double than in green banana. (Sample (3) and (4)). In addition, the quantity of volatiles, which were lost in osmotic dehydration of ripe banana, was found to be nearly double in green banana (sample (5) and (6)). Moreover, the fact that the loss of volatiles during air-drying of ripe sample was more significant (P<0.05) than in green banana (sample (1) and (2)) confirmed the role of changes of fruit structure on the retention of volatiles.
Figure 4.7: Comparison of volatile profiles of fresh banana, osmotic-air-dried banana, and of sucrose syrup (60%, 30°C) used in osmotic dehydration.
4.6.3 The effect of the length of osmotic pretreatment, and of sugar nature in the retention of volatiles

The effect of the length of osmotic pretreatment, and the sugar used on the retention of volatiles in subsequently air-dried samples was investigated. The results are shown in Table 4.12.

Table 4.12: Comparison of the effect of different osmotic conditions on the retention of volatile compounds in osmotic-air-dried bananas.

<table>
<thead>
<tr>
<th>Dehydration conditions</th>
<th>Examined Samples</th>
<th>Ratio of total peak area of fresh sample / total peak area of examined sample.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-drying</td>
<td>Ripe fresh banana</td>
<td>15.2</td>
</tr>
<tr>
<td>Osmotic-air drying</td>
<td>Sugar</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Osmotic dehydration duration (hours)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sucrose</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Glucose</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>Multi-dehydration</td>
<td>Air-drying 60 °C, 4 h + Osmotic 6h</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>Air-drying 80 °C, 2 h</td>
<td>Air-drying 60°C, 30 h</td>
</tr>
</tbody>
</table>

In all cases, the standard deviations in the mean ratios were 2-3% for 3 replications.
It can be seen that for both sucrose and glucose osmotic agents, six-hour contact with the fruit gave the best result for the maintenance of volatile banana components of the subsequent dried products. Twelve-hour osmotic dehydration gave the least effect. The length of the osmotic process dictated the relative importance of solute uptake and the loss of volatile compounds during osmotic process of ripe banana (refer to chapter 3). This, in turn had a strong effect on the loss of volatiles during drying.

The amount of solute uptake increased with the length of the osmotic process (the amount of solute uptake in ripe banana were 1, 2.4 and 3.2 % (w/w) for 2, 6, and 12 h osmotic dehydration respectively (sucrose 60% at 30°C).

It has been reported by some authors [96, 207-209] that aroma retention increases with increase in the soluble solid contents, because it decreased the diffusivity of volatiles (as well as of water). The results of this work seemed to disagree with the reports of these authors. This was most likely because of the greater leaching of fruit volatiles into the osmotic agent at longer contact times.

In summary, prolonging the length of osmotic dehydration did not improve the retention of volatiles in the dried product. A moderate length of osmotic dehydration gave the best result, because of greater solute uptake increased compared with shorter duration of osmotic dehydration, but before the loss of volatiles to the syrup during process became significant.
Sucrose was more effective than glucose in preventing the loss of volatiles in osmotic-air-drying of banana as shown in Table 4.12. Since sucrose has a higher molecular weight (MW) than glucose, it can act more effectively as a “molecular sieve” for the passage of moisture [96] as well as other components. As a result, the diffusion of sucrose into the osmotic samples made the diffusivity of volatiles out decrease more than in the glucose case. The decrease in the diffusivity of volatiles due to a “molecular sieve” effect of high MW solutes has been discussed by the other workers [96, 208].

Osmotic dehydration prior to air-dehydration showed its effect on reducing volatile loss for dried fruit. However, this effect was not very strong in the case of ripe banana due to extra loss of volatile during the osmotic process. A high initial drying rate was found to be very important in reducing drying time and to have a strong effect on the retention of volatiles. Therefore, a combination of air-drying at high initial rate prior to osmotic dehydration and followed by final air-drying might be able to further improve the volatile contents in the final air-drying banana. This could be carried out without much degradation of fresh banana volatiles, as seen in section 4.5.1, little qualitative change of banana volatile profile was found even drying at 90°C. The next section will discuss the effect of this multi-step drying regime.

4.6.4 The effect of multi-drying approach

Drying at a high temperature (80°C) prior to osmotic dehydration (6 hours, 60% sucrose syrup, 30°C) was carried out to obtain a high initial rate. Time for this initial
drying was short (2 hours), so that most of volatile components were not strongly affected by the high temperature. This is because at the beginning of drying, the material temperature is usually equal to the wet bulb temperature [68], for example at 200°C and RH = 0.8%, the wet bulb temperature is only 47°C [68].

To investigate the effect of a high initial rate, drying at 60°C prior to osmotic dehydration was also carried out for comparison with previous drying approaches. To obtain the same mass loss, drying was performed at 80°C for 2 hours and at 60°C was carried out for 4 hours. The results are shown in Table 4.12. Drying at high temperature prior to osmotic dehydration retained more volatiles. Drying at 60°C prior to osmotic dehydration was not so effective as osmotic dehydration alone.

It can be concluded that combined high-rate air-drying and osmotic dehydration showed the greatest volatile retention for dried banana. If banana was air-dried alone to 70% mass loss, the amount of banana volatiles decreased dramatically (by around 15 times), (P< 0.05). Whereas, applying this drying method, that reduction was only 2.5 times.

The initial high drying temperature had the effect of rapidly depleting water from the surface layer of banana and forming a hard surface layer. This in turn hindered the movement of moisture as well as volatiles. Therefore, after subsequent osmotic dehydration, the amount of volatiles lost in the sugar solution was also reduced. In addition to the effect on osmotic dehydration, this effect ensured the retention of volatile components.
Up to 90% aroma retention could be obtained in freeze drying [165] or spray drying [96] due to the application of a high initial drying rate. When the drying rate at the beginning is very high, an impermeable layer forms quickly and entraps volatiles in the dried product.

The natural distribution of banana volatiles also ensured the success of the “two-stage preconcentration” method. As stated in section 4.4, volatiles of banana were distributed unequally in the fruit; the center region containing a greater amount of volatiles than that of the surrounding tissue. As the result, the volatiles would be entrapped inside the banana during drying if there was a “barrier” which protected them.

Drying at 60°C prior to osmotic dehydration did not have such a significant effect on retaining volatiles in banana. It neither helped to reduce drying time nor formed a hard layer to prevent the loss of volatiles in both air-drying as well as in osmotic dehydration.

In general conclusion, osmotic dehydration prior to air-drying improved the retention of volatiles in dried product. Six-hour osmotic dehydration was found to be optimal to allow sufficient amount solute uptake, to assist in the retention of volatile in dried banana. However, loss of volatiles during the osmotic process of ripe banana was still considerable. To improve this matter, drying at high initial rate prior to osmotic dehydration was applied. Drying at 80°C was recommended for this short dehydration
Volatiles of osmotic-air-dried samples were found to be retained in the dried product for a very long time (more than 8 months).

4.7 SUMMARY

SPME in conjunction with GC and GC-MS has been shown to be suitable for the extraction, separation, and identification of volatile components of fresh banana, air-dried banana and osmotic-air-dried banana. A 100 μm PDMS fibre was the most effective for extracting banana volatiles. Over 100 compounds were found in fresh banana, and over 50 positively identified, of which esters were a major proportion. Most of these esters were acetates and butyrates. The identified compounds of fresh banana agreed with reports from literature and their amounts increased significantly in ripe banana. There was little evidence of any new compounds being formed during drying at temperatures of commercial drying (< 80°C) for banana.

The SPME technique was simple, and allowed rapid sampling and good reproducibility for monitoring volatile changes in dried banana. In this work, the precision of this technique was ~5% RSD. This value agreed well with Pawliszyn et al [194] for manual operation.

The loss of volatiles during drying was found to be strongly influenced by the initial drying rate. Therefore, drying at 80°C was best for reduced loss of volatiles. Under the
same drying conditions, the level of volatile loss was found dependent upon the characteristics of individual compounds, and upon their natural distribution in different parts of banana. In addition, the change of microstructure of banana with different maturity was found to affect the level of volatile loss.

Osmotic dehydration of banana prior to air-drying was found to be useful to reduce volatile loss. However, loss of volatiles in the osmotic solution was clearly observed during the osmotic process. Air-drying at high initial drying rate prior to osmotic dehydration was effective to help further retain volatiles during drying. This assured that if the appropriate drying condition was applied, loss of volatiles during drying could be reduced significantly, and controlled effectively.
CHAPTER FIVE

GENERAL CONCLUSION
There are several banana products presently trading in world market such as flakes, powder, puree, canned, chips, distilled essence, banana figs. Among these, dried bananas (figs or slices) might be the most common products as they are easy to consume. At present, there is no significant commercial production of dried banana in Australia. This thesis then, is the result of investigation into the improvement of the efficiency of the dehydration process, and the enhancement of dried banana in terms of flavour.

The process of drying is controlled by the properties of the air surrounding the product along with the properties of the product itself. At all drying temperatures examined in this study, drying was found to occur in the falling rate period, in which mass transfer is controlled by the concentration gradient of moisture inside the food matrix.

A simple model describing the drying kinetics was proposed based on Fick’s Second Law of diffusion. Mass transport was assumed to occur in one dimension and initial moisture content was assumed to be uniformly distributed throughout the fruit, and thus water diffusivity was considered to be independent from moisture content. Parameters required in the model were estimated from the values of equilibrium moisture contents. An empirical method for the estimation of equilibrium moisture contents gave the results of good agreement with literature. However, significant discrepancies were seen between the experimental equilibrium moisture contents and values, which were calculated from the well-known equations such as Henderson’s equation, and the GAB equation using the given constants in the literature. This might be due to large different humidities used in this work compared to the literature.
The values of moisture content as a function of drying time given in the model agreed well with the experimental data within a wide range of temperatures (30-70°C). Thus, this purely diffusion model would be valuable for predicting drying rates of banana (thin slice, 1cm). Some values of diffusivities agreed highly with the data in the literature.

Drying temperature was found to exhibit a profound effect, particularly on the initial drying rate. Temperature dependent diffusivity followed the Arrhenius type equation with high value of $R^2 = 0.99$.

All water diffusivities of 2 cm slabs were greater than that of 1 cm slabs suggesting that the movement of water in thick slabs may not be a one-dimensional diffusion and that a side-way movement might account for the faster removal of moisture in thick slabs. However, to ascertain this, further studies need to be carried out. Moreover, a more rapid surface hardening effect in thin slabs might result in the inhibition of water movement in thin slabs compared with thick slabs.

Drying rate was found to be similar between green and ripe banana for various temperatures and thickness. Increased sugar contents in ripe banana should lead to a decreased drying rate, and the more open structure of the ripe one should result in a faster drying rate. Thus, the combined effect might result in their equal drying rates.

A reasonable rate of dehydration (around 25% mass loss, in four hours) could be attained using optimal osmotic conditions (60% sucrose solution, at 30°C). The
subsequent air-drying of osmosed samples gave dried banana with better texture, colour, and flavour in comparison with products from air-drying alone.

The factors, such as temperature, immersion time, sugar nature and concentration of sugar solution, which affected the solute and moisture diffusion in osmotic dehydration of banana slices, were studied. These factors were not investigated separately, but the combined effects of these factors were focussed in this work. The aim was to ascertain the key role of temperature over other factors. As temperature can change the physical characteristics of sugar solution (viscosity, solubility) as well as fruit cell structure. In addition, chemical reactions (the hydrolysis of sucrose at high temperature) might occur in fruit as well as in the osmotic agent with increased temperature. These in turn might strongly affect both solute and water diffusion. This was proved by the fact that over the range of syrup concentrations examined in this work (30%- 60%), with osmosis at 30°C, and 40°C the use sucrose was found to favour faster mass loss and to limit solute uptake than using glucose. At 60°C the trend was reversed.

The decreased solute uptake in ripe banana compared with in green banana under the same osmotic conditions was observed. The leakage of solute from the fruit and solute uptake through osmosis may be the main reason of this drop. This loss has been from the expansion the intercellular spaces in ripe banana due to the collapse of cell walls. In addition, the fact that sugar content dramatically increased in ripe banana might account to the decrease of sugar concentration gradient between fruit and sugar solution, as a result, solute uptake would decrease in ripe sample.
The effect of sugar uptake on subsequent air-drying of banana has been seen clearly. The more sugar uptake in osmosis was, the slower the drying rate has been observed. However, due to high level of sugar in osmosed fruit, the dried product could have the better durable shelflife during storage, although drying can be stopped at a higher moisture content compared to the dried sample without this treatment.

Headspace solid-phase micro-extraction was applied for extraction of volatiles from fresh and processed bananas including air-drying samples with different drying conditions (temperature, thickness) and osmotic-air-dried bananas. Over fifty compounds of fresh banana were identified using GC-MS. Reproducibility of HS-SPME was good with most values of percent RSD being around 5%. These results showed that HS-SPME has potential as a routine method for analysing changes in key flavour compounds during different fruit processing regimes.

100 μm PDMS fibre was found to be the most effective for extracting banana volatiles. Sample equilibrium at high temperature was found to favour the best release of analytes from the food matrix into the headspace. This condition was combined with the SPME equilibrium at low temperature to attain the most effective sampling condition for banana volatiles.

Little evidence of new volatile compounds formed during the drying of banana might be because most banana volatile components were esters, which rarely undergo the common reactions in drying process such as Maillard or caramelisation. Due to these characteristics, it was interesting to find to what extent these compounds were lost.
during drying and what were the optimal drying conditions for reducing the loss of these compounds.

A high drying rate assisted the reduction of volatile loss during processing. This might be due to the reduction of time for fruit in contact with heat and the formation of a protecting layer on the surface of slabs, which helped to hinder the loss of volatiles. In addition, the preservation of microstructural of fruit tissue when drying at high temperature (for example porosity) might be one of the most important factors for the reduced loss of these compounds in fruit. This was consistent with the reports of other authors regarding drying banana [50, 51]. They found that drying at high temperature reduced the porosity most effectively. This reduction in turn also improved the retention of volatiles during process.

Osmotic dehydration prior to air-drying was found to improve the retention of volatiles in dried banana. The immersion time, maturity of banana and sugar nature, all affected that retention. In summary, the first two factors influenced volatile loss during processing due to the open structure in ripe banana. The third factor dictated a "sieve effect" reducing volatile loss.

The combination of air-drying at high temperature first, then osmotic dehydration at the optimal condition and air-drying thereafter at low temperature was found to greatly enhance retention of volatiles. This result was consistent with the remaining results in this work and might suggest an application in commercial production of dried fruit for the improvement of flavour quality.
Further work

To further elucidate the relationship between dehydration conditions and drying behavior and their effects on the product quality, the following further studies may be useful to further enhance the quality of dried fruit not only for banana, but also for other fruits.

• Thermal dehydration studies:

i) Further modelling of air-drying of banana taking into account the shrinkage is worthwhile investigating especially a comparison of the effect on different thickness slabs. This may assist to improve product appearance in commercial drying.

ii) The influence of drying conditions on the physical changes in fruit. This may help to control undesired changes in fruit during processing which can affect the product quality (texture and appearance).

iii) Applying pretreatment prior to drying to improve the colour of product without sulfiting.

• Further investigation of osmotic dehydration of banana (or other fruit) for the following issues:
i) The influence of osmotic conditions on product quality of dried banana. The present work found that osmotic dehydration using different osmotic agents resulted in a different colour and texture in osmotic-air-dried banana and perhaps a difference in product stability during storage (due to the difference in solute uptake). Further investigation of this matter may be of interest. This will be done with a variety of sugar types and forms (syrup or raw sugar). The influence of pH and temperature of sugar solution on osmotic process may also be investigated.

ii) Further investigation of the possible relationship between the level of sugar in fruit (i.e. the amount of total sugar and individual sugar changes during fruit ripening) and solute uptake in osmosis. This could be carried out using HPLC analysis of sugar contents in fresh fruit using samples in different maturity and corresponding osmosed samples.

- Further studies on the retention of banana volatiles of dried product:

i) Improvement of the extraction of banana volatile compounds applying the SPME technique with different types of fibres for the maximum extraction and quantitative analysis of various banana volatile components (due to their different polarity and volatility). This would compare the efficiency of this technique and traditional extraction techniques, in terms of the number of extractants, and accurately quantitative analysis.
ii) Applying a two-temperature model in air-drying banana to investigate the optimal conditions for retention of banana volatiles. This may yield practical applications in commercial drying if the optimal conditions for the retention volatiles are also a cost savings condition.

iii) The effect of pretreatment (for example blanching) prior to osmotic dehydration on the retention of banana volatiles may be interesting. This might ascertain further the role of microstructural change on the level of solute exchange during osmosis and the subsequent effect of solute uptake on volatile retention.

iii) Finally, it is interesting to find the optimal stage of maturity in banana, to produce dried banana, which has the best flavour.
REFERENCES


196. Supelco’s instruction for manual SPME device.


