1998

Chemical and physical changes during dehydration of prunes (Prunus domestica)

Henry T. Sabarez

University of Wollongong

Recommended Citation
NOTE

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.
CHEMICAL AND PHYSICAL CHANGES DURING DEHYDRATION OF PRUNES (PRUNUS DOMESTICA)

A thesis submitted in fulfilment of the requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

THE UNIVERSITY OF WOLLONGONG

by

HENRY T. SABAREZ (B.S., M.Eng.)

Supervisor: DR. WILLIAM E. PRICE

Department of Chemistry
November, 1998
To my wife, MERCEDES

and my children, HARRIET & MARC ...
ACKNOWLEDGEMENTS

I would like to express my deep appreciation to Dr. William E. Price, my adviser, for his assistance, encouragement and stimulating discussions. Indeed, his constructive suggestions helped sharpen many of the ideas established in this investigation. This work would not be completed without his efforts.

This study was also made possible through the assistance provided by the staff of the Chemistry Department. In particular, I wish to thank Prof. John Bremner for his helpful comments, Dr. John Korth and Larry Hick for their support in implementing the GC-MS work and Peter Pavlic for his technical assistance. Many thanks are due to Steve Cooper, Mick Weir, John Reay, John Forest & Peter Sarakiniotis for their help in the design and fabrication of the experimental drying system.

I wish to express my sincere thanks to Prof. Lawrie Woolf and Dr. Phil Back of ANU, Canberra for their valuable advice and for providing NMR diffusion data. Also, special thanks to Dr. Richard Storey of the CSIRO, Merbein, Victoria for furnishing SEM micrographs of plums. It is also my great pleasure to acknowledge the skill and expertise of Tom Rhymes and Marek Kaminski of ANU who assisted in the design and construction of the monitoring system.

I am very grateful for the assistance of the staff of the Young District Producers Cooperative (YDP), Young, N.S.W. especially to the Manager, Mr. Kelvin Cronk, for allowing me to use their prune processing facilities for field trials and for the provision of large amounts of fresh plums. The help and cooperation of all the workers at YDP plant sites, in particular, to Phil at Maimuru and Lee Dailey at Kingsvale are highly appreciated. I would like also to convey my gratitude to David Martin and his family for permitting me to conduct the pretreatment trials at their prune factory.

The Dried Fruits Research and Development Council (DFRDC) of the Federal Government of Australia is gratefully thanked for financial support.
Thanks to my colleagues in our laboratory for their help and friendship especially to Leanne W. Laarjoki, Hamish, and Kerry and to all my Filipino friends in Australia.

I am also indebted to my dear family (parents, brothers, sisters, father-in-law, mother-in-law, and brother-in-laws) for their constant support, love and prayers.

Finally, special thanks to my wife, Ching, for her love, patient and understanding and to my children, Harriet and Marc, for making my life cheerful and meaningful.

Above all, thanks to Almighty God for his unceasing blessings and guidance.
ABSTRACT

Prune is an important product in the dried fruit industry. The production of prunes involves drying of high-moisture fresh plums. Drying is an energy intensive food processing operation, which plays a significant role on the quality of the product. Increased competition in today's global market means that avenues to improve the process efficiency and product quality are desirable. In order to do this it is important to understand the physical and chemical changes occurring during drying.

Comprehensive physico-chemical investigations of the drying process of plums were conducted. This would help to establish a scientific basis for suggesting improvements to the commercial dehydration of plums with a view of maintaining or enhancing the quality of the dried product. A computer-based laboratory drier was designed and built to study the kinetics of drying plums under controlled conditions.

The effects of the process parameters (i.e., temperature, relative humidity and velocity) on the kinetics of moisture loss were studied to ascertain the major factors controlling the rate of drying plums. Results of the study showed a remarkable influence of the process parameters demonstrating the need for better control of the conditions of the drying air. These together with the ancillary experiments revealed that there may be different rate-controlling mechanisms involved during drying implicating an important role of the skin layer to moisture transfer. Notable differences between the drying curves of plums dried without skin and those with skin intact corroborated the importance of the skin layer to the drying process.

Modelling the drying process has also provided more insight into the mechanisms of mass transfer during drying under different conditions. The proposed models predicted well the drying curves and could serve as descriptive tools in predicting the drying process of plums. This is important for the optimisation process. In addition, the study of using chemical pretreatment based on fatty acid esters further disclosed the significant effects of the skin layer to moisture loss during drying. It showed that dipping pretreatment can be employed to enhance the drying process of plums depending upon the composition of the drying emulsions and the drying conditions.
The approach of monitoring the kinetics of changes in the carbohydrate constituents of plums using HPLC has shown dramatic alterations in the amounts of the major carbohydrates present in plums (i.e., fructose, sorbitol, glucose and sucrose) during drying and storage. It unveiled the major carbohydrate degradations occurring during drying including the hydrolysis of sucrose, Maillard reactions and caramelisation. Drying conditions and the pH of the fruit were found to affect the rate and onset of these reactions. The study shows the usefulness of the approach in detecting the progress of the chemical degradation reactions and further manifests the importance of controlling the conditions during drying of plums.

It is known that the decomposition of carbohydrates would lead to the generation of wide spectrum of volatile flavours depending upon the type of reaction. A solid-phase microextraction (SPME) technique in conjunction with GC-MS was used to characterise and follow the changes of volatile flavours during drying of plums. The study of aroma profiling showed significant changes to the volatile constituents of plums during drying identifying relevant routes leading to the formation of the volatile flavours associated with the carbohydrate degradations. The result demonstrates the importance of aroma profiling in diagnosing further the progress of the chemical degradation reactions, which has important implications for the control of the quality of the product.

The impetus of controlling the drying process manifests the need for better knowledge of the conditions in which the fruits are experiencing during commercial dehydration. This information is also important for simulating the commercial drying conditions in laboratory studies. In this respect, a computer-based data acquisition system was developed to monitor the conditions during commercial dehydration of prunes. The monitoring work was found to be useful in identifying anomalies in drying conditions in the tunnel exemplifying the utility of the device in assessing the performance of the tunnel.


CONTENTS

DECLARATION i
ACKNOWLEDGEMENTS ii
ABSTRACT iv
PUBLICATIONS vi
CONTENTS vii
LIST OF TABLES xii
LIST OF FIGURES xiii

CHAPTER 1  INTRODUCTION 1

1.1  Background Review 2
1.2  The d’Agen Plum 4
   1.2.1  Physical Characteristics 4
   1.2.2  Morphological Structure 5
   1.2.3  Chemical Composition 6
      1.2.3.1  Carbohydrates 6
      1.2.3.2  pH 7
      1.2.3.3  Volatile Flavours 8
      1.2.3.4  Other Matter 9
1.3  The Production of Dried Prunes 10
1.4  The Drying Process 13
   1.4.1  Water in Foodstuffs 13
   1.4.2  Drying Mechanisms 15
1.5  Effects of Drying on Product Quality 21
   1.5.1  Thermal Degradation of Carbohydrates 22
   1.5.2  Volatile Formation during Drying 25
1.6  Aims of this Research 28
CHAPTER 2  THE KINETICS OF MOISTURE TRANSPORT
DURING DRYING OF PLUMS

2.1  Introduction 32

2.2  Experimental 33

2.2.1  Materials 33

2.2.2  Preliminary Batch Drying Experiments 34

2.2.3  Design and Development of an Improved Experimental Dehydration System 35

2.2.4  Instrumentation 39

2.2.4.1  Measurement of Fruit Temperature Profiles during Drying 39

2.2.4.2  Measurement of Air Velocity 39

2.2.5  Drying Procedures 39

2.2.6  Moisture Content Determination 40

2.3  Results and Discussion 40

2.3.1  Preliminary Drying Experiments 40

2.3.2  Performance of the Improved Experimental Dehydration System 43

2.3.3  Effect of Process Parameters on Drying Kinetics 45

2.3.3.1  Drying Air Temperature 45

2.3.3.2  Drying Air Velocity 48

2.3.3.3  Drying Air Relative Humidity 50

2.3.3.4  General Discussion 52

2.3.4  Measurement of Fruit Skin Permeability and Water Mobility within the Fruit Flesh 57

2.3.5  Water Loss Profile during Ambient Storage 65

2.3.6  Influence of Initial Moisture Content on the Drying Kinetics of Plums 66

2.4  Conclusions 67
### CHAPTER 3  MODELLING THE DRYING PROCESS OF PLUMS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Introduction</td>
<td>69</td>
</tr>
<tr>
<td>3.2 Two-Regime Drying Model</td>
<td>70</td>
</tr>
<tr>
<td>3.2.1 Model Formulation</td>
<td>73</td>
</tr>
<tr>
<td>3.2.2 Estimation of Model Parameters</td>
<td>75</td>
</tr>
<tr>
<td>3.2.3 Results of the Estimation of Model Parameters</td>
<td>78</td>
</tr>
<tr>
<td>3.2.4 Evaluation of the Two-Regime Model</td>
<td>87</td>
</tr>
<tr>
<td>3.3 Diffusion Drying Model</td>
<td>95</td>
</tr>
<tr>
<td>3.3.1 Development of Diffusion Drying Model</td>
<td>96</td>
</tr>
<tr>
<td>3.3.2 Determination of the Parameters in the Diffusion Model</td>
<td>104</td>
</tr>
<tr>
<td>3.3.3 Estimation of the Effective Diffusion Coefficient ($D_{eff}$)</td>
<td>106</td>
</tr>
<tr>
<td>3.3.4 Testing and Evaluation of the Diffusion Model</td>
<td>111</td>
</tr>
<tr>
<td>3.4 Conclusions</td>
<td>118</td>
</tr>
</tbody>
</table>

### CHAPTER 4  INFLUENCE OF CHEMICAL PRETREATMENT ON THE KINETICS OF DRYING PLUMS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Introduction</td>
<td>120</td>
</tr>
<tr>
<td>4.2 Effect of Fatty Acid Emulsions on the Drying Kinetics of Plums</td>
<td>121</td>
</tr>
<tr>
<td>4.3 Effect of Commercial Dipping Oil on the Drying Kinetics of Plums</td>
<td>123</td>
</tr>
<tr>
<td>4.4 Effect of Chemical Pretreatment at Different Drying Conditions</td>
<td>127</td>
</tr>
<tr>
<td>4.4.1 Drying Air Temperature</td>
<td>131</td>
</tr>
<tr>
<td>4.4.2 Drying Air Velocity</td>
<td>132</td>
</tr>
<tr>
<td>4.4.3 Drying Air Relative Humidity</td>
<td>133</td>
</tr>
<tr>
<td>4.5 Effect of Dipping Pretreatment on the Fruit Skin Permeability</td>
<td>134</td>
</tr>
<tr>
<td>4.6 Effect of Pretreatment on the Rate of Water Loss during Ambient Storage</td>
<td>135</td>
</tr>
<tr>
<td>4.7 Commercial Scale Testing of the Dipping Pretreatment Method</td>
<td>137</td>
</tr>
<tr>
<td>4.8 Conclusions</td>
<td>140</td>
</tr>
</tbody>
</table>
CHAPTER 5  THE KINETICS OF CARBOHYDRATE CHANGE
DURING DRYING OF PLUMS

5.1  Introduction
5.2  Materials and Methods
  5.2.1 Preparation of Dried Fruit Sample
  5.2.2 Sample Preparation for Sugar Analysis
  5.2.3 High-Performance Liquid Chromatography (HPLC) Analysis
  5.2.4 pH Determination
5.3  Results and Discussion
  5.3.1 Carbohydrate Content of d’Agen Plums
  5.3.2 Changes in Carbohydrate Content during Drying
  5.3.3 Effect of Process Parameters on the Kinetics of Carbohydrate Change during Drying
    5.3.3.1 Influence of Drying Air Temperature
    5.3.3.2 Influence of Drying Air Velocity
    5.3.3.3 Influence of Drying Air Relative Humidity
  5.3.4 Degradation By-products
  5.3.5 Effect of Fruit pH on the Kinetics of Carbohydrate Change during Drying
  5.3.6 Carbohydrate Content of Commercially Dried Prunes
  5.3.7 Changes in Carbohydrate Contents of Dried Prunes during Ambient Storage
5.4  Conclusions

CHAPTER 6  IDENTIFICATION AND MONITORING OF VOLATILE CONSTITUENTS IN PLUMS DURING DRYING USING SOLID PHASE MICROEXTRACTION (SPME) IN CONJUNCTION WITH GAS CHROMATOGRAPHY - MASS SPECTROMETRY (GC-MS)
<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Estimated model parameters for the proposed two-regime model</td>
<td>84</td>
</tr>
<tr>
<td>3.2</td>
<td>General data used for the diffusion model</td>
<td>104</td>
</tr>
<tr>
<td>3.3</td>
<td>Estimated effective diffusion coefficient ($D_{eff}$) [Rh=3%; $V=5$ m/s]</td>
<td>110</td>
</tr>
<tr>
<td>4.1</td>
<td>Effect of dipping pretreatment (2% K$_2$CO$_3$ + 2.5% Voullaires oil) under different drying conditions on the total drying time (Final MC = 20% dry basis)</td>
<td>131</td>
</tr>
<tr>
<td>4.2</td>
<td>Final moisture content (% dry basis) of untreated and pretreated plums dried in parallel-flow commercial prune dehydrator</td>
<td>141</td>
</tr>
<tr>
<td>6.1</td>
<td>Gas chromatography - mass spectrometry (GC-MS) analysis parameters</td>
<td>188</td>
</tr>
<tr>
<td>6.2</td>
<td>Reproducibility of the headspace SPME technique from blended fresh plum samples using 100µm polydimethylsiloxane-coated fibre</td>
<td>194</td>
</tr>
<tr>
<td>6.3</td>
<td>Qualitative changes in the volatile components of plums during drying (T=80°C; Rh=3%; $V=5$ m/s)</td>
<td>200</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

1.1 The d’Agen Plum 4
1.2 SEM micrograph of cross section of the freeze-fractured skin layer of the plum [magnification: x2500] (Storey and Price\textsuperscript{119}) 5
1.3 Typical processing concept for the production of prunes 10
1.4 Schematic diagram of the commercial prune tunnel dehydrators 12
1.5 Typical drying rate curve for a food product (adapted from Heldman and Hartel\textsuperscript{54}). 17
1.6 Chemical structure of carbohydrates 23

2.1 Schematic diagram of the experimental dehydration system 35
2.2 Flow chart of the automated data collection process 38
2.3 Effect of drying air temperature on the kinetics of drying plums using conventional air oven (Rh<5%; V<0.3 m/s) 41
2.4 Effect of relative humidity of the drying air on the kinetics of drying plums using conventional air oven (T=80°C; V<0.3 m/s) 42
2.5 Relative humidity changes of the drying air at 80°C using the conventional air oven (V<0.3 m/s) 42
2.6 Typical drying data obtained using a computer-based experimental dehydration system (V=1 m/s; MC\textsubscript{iwb}=69%) 44
2.7 Effect of drying air temperature on the kinetics of drying plums (V=1 m/s; Rh=3%; MC\textsubscript{iwb}=69%) 46
2.8 Effect of air velocity on the kinetics of drying plums (T=70°C; Rh=3%; MC\textsubscript{iwb}=69%) 48
2.9 Effect of air relative humidity on the kinetics of moisture loss during drying of plums (T=70°C; V=1 m/s; MC\textsubscript{iwb}=69%) 51
2.10 Effect of air temperature on the rate of drying (V=1 m/s; Rh=3%; MC\textsubscript{iwb}=69%) 53
2.11 Maximum evaporation rate from free water and plums at different air temperatures (Rh=3%; V=1 m/s) 54
2.12 Effect of the waxy skin layer of plums on the drying kinetics (T=70°C; Rh=3%; V=1 m/s; MC_{iwb}=69%) 55

2.13 Surface temperature profile of plums during drying at various air temperatures (Rh=3%; V=1 m/s) 56

2.14 Schematic diagram of the radiotracer setup 57

2.15 Effect of drying on water permeability of plum skin using radiotracer method (T=70°C; Rh=3%; V=5 m/s) 59

2.16 Surface temperature profile of plum dried at 70°C (Rh=3%; V=5 m/s) 60

2.17 Diffusion coefficient of water in plums obtained from NMR spin-echo technique (Back and Price105) 61

2.18 Mobility of water through the skin of plums obtained from the radiotracer results at 25°C 63

2.19 The rate of mass loss during ambient storage of plums partially dried at different temperatures and times (Rh=3%; V=5 m/s; MC_{iwb}=66%) 66

2.20 Effect of initial moisture content on drying kinetics of plums (T=70°C; Rh=3%; V=1 m/s) 67

3.1 Surface and centre temperature profiles of plums during drying (T=70°C; Rh=3%; V=1 m/s; MC_{iwb}=69%) 79

3.2 Plum temperature profile during drying at different relative humidity conditions (T=70°C; Rh=3%; V=1 m/s; MC_{iwb}=69%) 80

3.3 Plum temperature profile during drying at different air temperatures (Rh=3%; V=1 m/s; MC_{iwb}=69%) 80

3.4 Typical plot of ln (T_{a}-T) versus time for the estimation of heat transfer coefficient (h) at different temperatures using fruit surface temperature (Rh=3%; V=1 m/s; MC_{iwb}=69%) 82

3.5 Plum centre temperature profile during drying at 90°C (Rh=3%; V=1 m/s; MC_{iwb}=69%) 82

3.6 Illustrative example of the plot for the estimation of critical point (Rh=3%; V=1 m/s; MC_{iwb}=69%) 83
3.7 Plots for the moisture loss during drying of plums at different temperatures expressed as a first-order rate process (Rh=3%; V=1 m/s; MC_{iwb}=69%)  
88

3.8 Temperature dependence of rate of plum drying in terms of Arrhenius plot (Rh=3%; V=1 m/s; MC_{iwb}=69%)  
89

3.9 Experimental drying data fitted to first-order kinetics model (Rh=3%; V=1 m/s; MC_{iwb}=69%)  
90

3.10 Comparison between the experimental mass loss data and the predicted values at different humidity conditions (T=70°C; V=1 m/s; MC_{iwb}=69%)  
91

3.11 Comparison between the experimental mass loss data and the predicted values at different air temperatures (Rh=3%; V=1 m/s; MC_{iwb}=69%)  
93

3.12 Comparison between the experimental drying rate and the predicted values at different air temperatures (Rh=3%; V=1 m/s; MC_{iwb}=69%)  
94

3.13 Schematic diagram of the plum used for diffusion model  
96

3.14 Changes in volume of plums during drying as a function of moisture content (T=80°C; Rh=3%; V=5 m/s; MC_{iwb}=66%)  
105

3.15 Radial change in plums during drying as a function of time at different drying temperatures (Rh=3%; V=5 m/s; MC_{iwb}=66%)  
106

3.16 Semi-log plots of the experimental moisture ratio (MR) against time at different drying temperatures (Rh=3%; V=5 m/s; MC_{iwb}=66%)  
108

3.17 Arrhenius plot of the effective diffusion coefficient versus inverse absolute temperature (Rh=3%; V=5 m/s; MC_{iwb}=66%)  
109

3.18 Comparison between experimental and predicted moisture content profiles of plums during drying at 80°C (Rh=3%; V=5 m/s; MC_{iwb}=66%)  
112

3.19 Comparison between experimental and predicted moisture content profiles of plums during drying at 70°C (Rh=3%; V=5 m/s; MC_{iwb}=66%)  
113
3.20 Comparison between the experimental and predicted drying kinetics of plums with and without skin (T=70°C; Rh=3%; V=1 m/s; MCiwb=66%)

3.21 Semi-log plots of the experimental moisture ratio (MR) versus time for plums dried with and without skin (T=70°C; Rh=3%; V=1 m/s; MCiwb=66%)

3.22 Predicted moisture content distribution within the plum during drying at 80°C (Rh=3%; V=5 m/s; MCiwb=66%)

4.1 Effect of different dipping pretreatments on the rate of drying plums (T=70°C; Rh=3%; V=1 m/s; MCiwb=69%)

4.2 Effect of different dipping pretreatments on the drying kinetics of plums (T=70°C; Rh=3%; V=5 m/s; MCiwb=66%)

4.3 Effect of different dipping pretreatments on the rate of drying plums (T=70°C; Rh=3%; V=5 m/s; MCiwb=66%)

4.4 Effect of dipping pretreatment (2.5% K₂CO₃ + 2.5% Voullaires oil) on plum skin permeability using radiotracer method

4.5 Effect of pretreatment (2% K₂CO₃ + 2.5% Voullaires oil) on the rate of mass loss during ambient storage of partially dried plums (T=70°C; Rh=3%; V=5 m/s; MCiwb=66%)

4.6 Effect of pretreatment (2% K₂CO₃ + 2.5% Voullaires oil) on the rate of mass loss during ambient storage of partially dried plums (T=80°C; Rh=3%; V=5 m/s; MCiwb=66%)

5.1 Schematic diagram of the experimental HPLC system and the conditions employed

5.2 HPLC chromatogram of fresh plums (1) fructose, (2) sorbitol, (3) glucose and (4) sucrose

5.3 HPLC chromatogram of 12000 ppm standard sugar solution (1) fructose, (2) sorbitol, (3) glucose and (4) sucrose

5.4 Example of the standard calibration curve for glucose component
5.5 Carbohydrate composition of fresh plums obtained during the 1996 and 1997 picking seasons

5.6 Carbohydrate changes in plums during drying at 80°C (Rh=3%; V=5 m/s; MC_{iwb}=66%)

5.7 Non-enzymatic browning scheme (Nursten\textsuperscript{82})

5.8 Carbohydrate changes in plums during drying at 70°C (Rh=3%; V=5 m/s; MC_{iwb}=66%)

5.9 Carbohydrate changes in plums during drying at 70°C (Rh=3%; V=1 m/s; MC_{iwb}=66%)

5.10 Average fruit temperature profile during drying at different air velocities (T=70°C; Rh=3%)

5.11 Carbohydrate changes in plums during drying at 70°C (Rh=30%; V=1 m/s; MC_{iwb}=66%)

5.12 HPLC chromatogram of plums dried at 80°C (Rh=3%; V=5 m/s) for 18 hours; (1) fructose, (2) sorbitol, (3) glucose, (4) sucrose and (5) degradation peak

5.13 Changes in carbohydrate content of plums with pH of 3.63 (+0.21) during drying at 90°C (Wilford\textsuperscript{14})

5.14 Changes in carbohydrate contents of plums with pH of 4.83 (+0.11) during drying at 90°C

5.15 Carbohydrate contents of commercially dried prunes using different methods of drying

5.16 Changes in carbohydrates of plums dried at 70°C (Rh=3%; V=5 m/s) for up to 20% moisture content (dry basis) during ambient storage

6.1 Schematic diagram of the Solid Phase Microextraction (SPME) device

6.2 GC-MS chromatogram of the headspace flavour constituents of fresh blended plums extracted using 100\textmu m polydimethylsiloxane-coated SPME fibre
6.3 Mass spectrum of hexenal in comparison with that from NSB library collection

6.4 GC-MS chromatogram of the headspace blank run using 100µm polydimethylsiloxane-coated SPME fibre

6.5 GC-MS chromatogram of the headspace flavour constituents of whole fresh plums extracted using a 100µm polydimethylsiloxane-coated SPME fibre

6.6 GC-MS chromatogram of the headspace flavour constituents of plums dried at 80°C (Rh=3%; V=5 m/s) for (a) 1 hour, (b) 9 hours and (c) 18 hours extracted using 100µm polydimethylsiloxane-coated SPME fibre

6.7 Mass spectrum of 2-furancarboxaldehyde in comparison with that from NSB library collection

6.8 Changes in the amount of nonanal constituent of plums during drying at 80°C (Rh=3%; V=5 m/s)

6.9 Changes in the amount of TMCHB constituent of plums during drying at 80°C (Rh=3%; V=5 m/s)

6.10 Changes in the amount of benzaldehyde constituent of plums during drying at 80°C (Rh=3%; V=5 m/s)

6.11 Hydrolysis of amygdalin (Davidek et al36)

6.12 Changes in the amount of 2-furancarboxaldehyde constituent of plums during drying at 80°C (Rh=3%; V=5 m/s)

6.13 Caramelisation of glucose in acidic degradation (Hurrell83)

6.14 Typical caramel aromatics (Kroh87)

6.15 GC-MS chromatogram of the headspace flavour constituents of plums dried at 70°C (Rh=3%; V=5 m/s) for 18 hours extracted using 100µm polydimethylsiloxane-coated SPME fibre

7.1 Schematic diagram of a parallel-flow tunnel dehydrator and the position of the monitoring system

7.2 Cross-sectional position of the monitoring sensors in the tunnel dehydrator
7.3 Monitoring system at work in the commercial dehydrator at Maimaru, Young, NSW

7.4 Temperature and humidity profiles of the drying air in parallel-flow tunnel at the inlet section 100 cm from the wall (Set temperature: 84°C)

7.5 Temperature and humidity profiles of the drying air in parallel-flow tunnel at the central section 100 cm from the wall (Set temperature: 84°C)

7.6 Temperature and humidity profiles of the drying air in parallel-flow tunnel at the outlet section 100 cm from the wall (Set temperature: 84°C)

7.7 Cross-sectional temperature profile of the drying air in the tunnel dehydrator (Set temperature: 84°C; top section)

7.8 Cross-sectional relative humidity profile of the drying air in the tunnel dehydrator (Set temperature: 84°C; top section)

7.9 Longitudinal temperature profile of the drying air in the tunnel dehydrator at different heights (Set temperature: 84°C; 100 cm from the wall)

7.10 Longitudinal relative humidity profile of the drying air in the tunnel dehydrator at different heights (Set temperature: 84°C; 100 cm from the wall)

7.11 Temperature profile of the drying air in the tunnel as a function of height at different sections (Set temperature: 84°C; 100 cm from the wall)

7.12 Relative humidity profile of the drying air in the tunnel as a function of height at different sections (Set temperature: 84°C; 100 cm from the wall)
Chapter 1

INTRODUCTION
Chapter 1

1.1 BACKGROUND REVIEW

Prunes are an important product for the dried fruit industry. There are flourishing industries of commercial significance in several countries. In 1996, the worldwide production of dried prunes was reported by the International Prune Association (IPA) to be about 275000 metric tons. The major prune-producing countries in the world include USA, France, Chile, Argentina and Turkey. Australia has a small prune industry with an annual production of up to 4500 tonnes of dried product. The majority of the produce is consumed domestically. The main prune-growing areas are concentrated in Young and Griffith districts of New South Wales.

The processing of prunes usually relies on drying of fresh plums. Drying is considered a major energy-consuming operation in the production of prunes. It is one of the crucial operations having influence on the quality of the product. Normally, commercial drying of prunes is carried out in long dehydration tunnels, and energy costs during such process account for a major portion (about 30%) of the total production costs. Increased competition in today's global market means that avenues to improve the efficiency of the dehydration process are desired.

Enhanced energy efficiency may be achieved through better understanding of the mechanisms involved during drying. Drying is the removal of solvent, generally water for most kinds of foodstuffs, from solids by thermal means. Although the attainment of a low water activity through moisture loss to inhibit microbial action is the main reason for drying, other considerations are often important. It is, for example, performed to minimise transport and handling costs. Due to the importance of drying there is a need to understand the controlling transport mechanisms, as these will affect the process efficiency as well as the product quality. The process of drying is controlled by the properties of the air surrounding the product along with the properties of the product itself. An understanding of these factors is therefore a key to a full assessment of the drying process.

Product quality is another important aspect that needs to be addressed with the energy conservation. To understand the quality changes that occur during drying, it is of
considerable interest to identify the chemical changes occurring during different stages of drying. The quality impairment usually encountered is the result of complex chemical reactions in the food and takes place at a rate, which strongly influenced by the drying conditions and properties of food product. However, still less is known about the extent of these effects on the quality of the product. In drying, this is important because the temperature and moisture content of the product are changing. Temperature and water content are known to greatly affect the chemical degradation reactions in foodstuffs. Another aspect is the vulnerability of the dried product to further chemical degradation that could occur during storage. It is thus far evident that there is always a race between the efficiency of drying and quality deterioration. Therefore knowledge of product quality change with drying conditions would help in devising an optimal drying process and in developing effective control paradigms.

The work undertaken in this research will address the above issues by increasing our basic understanding of the mechanisms controlling the rate of drying plums. This will involve extensive investigations of the factors affecting the rate of moisture loss including the effect of process parameters on drying kinetics and analysis of the water permeability through the skin and the rate of water movement within the fruit matrix. The results will be utilised to develop a physical model to obtain a clearer understanding of the mechanisms controlling the rate of drying and to provide a predictive tool for the drying of plums. The influence of chemical pretreatment to enhancing the rate of drying will also be looked in detail. Monitoring the carbohydrate changes during drying will be carried out to assist in establishing the chemical degradation reactions the plum undergoes during drying. Analysis of the volatile flavour profile during drying will be followed to further enhance our understanding of the chemical degradations that are taking place. These will contribute towards establishing a benchmark for quality control. It is therefore envisaged that this study will contribute towards revised efficient drying system, which could be employed to obtain better quality-dried product.
1.2 THE D'AGEN PLUM

1.2.1 Physical Characteristics

The plum is a widely cultivated stone fruit, which belongs to the Rosaceae family and of the genus Prunus. There are more than 2000 cultivars of plums, of which relatively few are of commercial importance. The d’Agen, a cultivar of the Domestica subspecies is the most commonly grown plum variety intended for drying (Figure 1.1). It is typically smaller than the common eating varieties weighing between 10 to 30 grams. This variety of plum is usually in oval shape. The skin color of mature plums varies from dark red to purplish depending upon the degree of maturity. It can not be stored for a long period under ambient condition: for this reason they are immediately dried.

Figure 1.1. The d’Agen Plum.
1.2.2 Morphological Structure

Plums are drupes characterised by a thin skin (epicarp), an edible fleshy pulp (mesocarp) and a highly lignified solid stone (endocarp). The endocarp consists of a single seed enclosed by a hard stone consisting of thick, lignified cell walls (sclerenchyma). The flesh surrounds the hard pit. The edible fleshy portion of the fruit comprises of basic structural units called parenchyma cells. Each parenchyma cell is enclosed in its own cell wall and bound together with other cells. It contains an active protoplast where all metabolic processes occur. The flesh portion also consists of phloem, xylem and collenchyma cells. All these cells are grouped together to form tissues. The parenchyma cells are the chief types of cells in plants, which are thin-walled and polygonal in shape and forms as the structural units of most parts of plants. The internal structure of the parenchyma cells usually functions as storage of water and reserves foods such as starch. They are living cells and form the primary tissues in the edible fleshy portion of fruits.

Figure 1.2. SEM micrograph of cross section of the freeze-fractured skin layer of plum [magnification: x2500] (courtesy by Storey and Price).
The skin of the plum consists of layers of elongated living cells (epidermis). It protects the underlying tissue and permits the exchange of metabolites with the environment. Wax is deposited on the outer surface of the skin layer. This wax forms a light-grey bloom and makes the skin impermeable to water. Figure 1.2 shows the cross-section of the skin layer. The skin layer of plum is important in its processing since it influences the rate of water movement during drying. An early attempt to relate the structure of the waxy surface of plums with their drying characteristics was made by Bain and McBean. These authors found a significant influence of the waxy skin layer to retard water loss during drying. Bain and McBean followed the development of the cuticular wax layer in plums and their changes occurring during drying and observed significant changes in the fine structure.

1.2.3 Chemical Composition

1.2.3.1 Carbohydrates

Carbohydrates are significant components in plums and amounts are found to vary between cultivars. Plums are known to contain three major simple carbohydrates: glucose, fructose and sucrose. The carbohydrate composition of different cultivars of plums has been studied previously. Forni et al examined the sugar contents of 13 cultivars of plums. They obtained total amounts of sugar ranged from 8.04% to 14.7% with the mean values for fructose, glucose and sucrose of 2.46%, 4.37% and 3.88%, respectively. Belitz and Grosch reported an average total sugar content of plum/prune of around 7.8% of fresh edible portion of which 1.3% is fructose, 3.55% is glucose and 1.5% is sucrose. Willis and co-workers reported the carbohydrate content of plum of which 1.7% is fructose, 2.1% glucose and 1.7% sucrose. Das Mohapatra and Sharma studied the chemical characteristics of 12 cultivars of plums and found the total sugars in the range 6.16% to 8.96%. However, none of these studies were conducted on d'Agen variety. The work of Wilford and Newman were the only information available on the sugar contents of d'Agen plums. Wilford found that the d'agen fresh plums contained total sugars of 9.5%, with fructose of 2.48%, glucose of
4.1% and 2.9% sucrose. The total sugars of the same cultivar were also reported by Newman\textsuperscript{15} to be about 20-25%.

Sorbitol is reported to be abundant in the fruits of the Rosaceae family such as pome and stone fruits.\textsuperscript{10} Several authors have reported the presence of sorbitol in plums. Working on d’Agen variety, Wilford\textsuperscript{14} detected the presence of the sugar alcohol sorbitol at about 4% (wet weight). Forni et al\textsuperscript{9} also reported the presence of sorbitol in 13 cultivars with the amounts ranged from 1% to 5.33%. They indicated that the sorbitol content is directly related to the total sugar content. Weiss and Samaun\textsuperscript{16} found 1.8% to 13.5% sorbitol in plum juices and Wrolstad and Shallenber\textsuperscript{17} obtained a sorbitol content of plums in the range of 0.6% to 2.01% of fresh weight. A small amount of sorbitol which is about 0.6% of the edible flesh portion has also been reported by Willis\textsuperscript{12} in plums. Kesley plum was found to contain about 2.8% sorbitol most of which is accumulated during the later part of growth cycle.\textsuperscript{18} The amount of sorbitol present in plums has been observed to be approximately the same as sucrose by Bollard.\textsuperscript{19} However, Hartmann\textsuperscript{20} observed that the sorbitol content increased with ripening and was inversely correlated with the sucrose content.

1.2.3.2 pH

The pH of the fruit is one of the important parameters that affect various chemical reactions known to occur during processing and storage. In plums, the pH has been widely reported for a number of cultivars. Belitz and Grosch\textsuperscript{10} have reported a plum pH of about 3.3. However, they did not mention the cultivars in which the pH measurement was made. Wani et al\textsuperscript{21} investigated the pH of three plum varieties and reported the values to be between 3.04 to 3.12. Six different plum cultivars were examined by Barbanti et al\textsuperscript{22} and found the pH values to vary from 3.4 to 3.8. Barbanti et al\textsuperscript{23} compared the pH of 12 cultivars of plums and reported the values to be in the range of 3.1 to 3.7. However, the d’agen variety of plums was not included in these studies. Wang et al\textsuperscript{24} reported the pH of Stanley plum paste to be about 3.45. The chemical properties of Santarosa plum variety was studied by Joshi et al\textsuperscript{25} and reported the pH to be 3.3. Vyas and Sharma\textsuperscript{26} also studied the pH of the same variety and found to vary
from 2.92 to 3.5. The only information available on the pH of d’Agen plums was that from Wilford\textsuperscript{14} who obtained an average value of about 3.63. The above reviews indicated that important differences in pH exist among cultivars. It is expected that the pH may vary between picking seasons due to natural variation in climatic conditions.

1.2.3.3 Volatile Flavours

The composition of volatile flavours of plums has been previously studied. As reported by Crouzet et al\textsuperscript{4}, over 280 different volatile constituents have been identified in aromatic extracts by several researchers. These were obtained from various plum cultivars using different techniques. Crouzet et al\textsuperscript{4} also pointed out that alcohols, esters or aldehydes were claimed by these authors to be quantitatively the major components of aromatic extracts of the plums. None of these alcohols or esters however exhibit the aromatic flavour resemblance to that of the plum. Williams and Ismail\textsuperscript{27} studied the volatile composition of plums by a sniffing method and detected some odorous compounds reminiscent to that of fresh plums. They found that regions containing with mixtures of linalool, benzaldehyde, ethyl nonanoate, methyl cinnamate and γ-decalactone were associated with the fresh plum-like aromas. Some other compounds suspected to contribute to the aroma of the fruit were also examined by the same authors who reported that nonanal, cis-hex-3-en-1-ol, γ-octalactone and hexan-1-ol could be considered as contributors to the aroma of the plums studied. Ismail\textsuperscript{28} concluded that the high scores on sensory impact were positively correlated with the concentrations of benzaldehyde, methyl cinnamate, γ-decalactone and 2-phenylethanol, and negatively related with the amount of hexanal. Increase in the concentration of hexenal was also concluded by Williams and Ismail\textsuperscript{27} to overpower the positive characteristics aroma of plums. Ismail et al\textsuperscript{29} examined the headspace aroma components of four cultivars of intact plums using gas chromatography - mass spectrometry (GC-MS) and found that all extracts were dominated by hexanol and nonanal. Nonanal, associated with the composition of the cuticular waxes of the plum, was described as woody, fragrant and mandarin-like odour. However, these authors observed that the aromas of four cultivars differed only in their quantitative composition. The presence of hydrocarbon compounds has also been reported to be associated with the wax properties of the skin of the plums.
Gomez et al\textsuperscript{30} found hydrocarbons to be prevalent in the extracts of the plums using simultaneous distillation extraction and analysed by GC-MS. Among the important volatile constituents they also identified C\textsubscript{6} compounds such as hexanal, 2-hexenal, hexanol and their esters. Most of these studies pointed out that enzymatic oxidation during sample preparation (i.e., milling) may result to the deterioration of aroma. Aromatic substances are often present in the raw material in their free or bound form. The bound form of compounds is usually released during food preparation.

Maturity has been reported to influence the volatile flavour compositions of the fruit. Dirninger-Rigo\textsuperscript{31} quantified the volatile constituents in half-ripe, ripe and overripe Mirabelle plums and found that aldehyde concentration decreased with maturity except nonanal. The decrease of these compounds particularly the C\textsubscript{6} saturated and unsaturated aldehyde, which are classified to exhibit green and pungent odours, was implicated to favour an increase in the quality of ripe plum aroma. They also observed that hydrocarbons became less abundant in mature fruit. Most of the terpene alcohols were also found to increase with maturity. The increase in the concentration of lactones was noted to be the most dramatic modification with maturity as these compounds were observed to be at 77 times higher concentrations in ripe than in half-ripe fruit. The amount of linalool was first observed to increase until normal maturity and then decreased quickly after normal maturity. The build-up of aromatic compounds during maturity was reported to be affected by external conditions.\textsuperscript{10} It is also generally recognised that the composition of fruit aroma varies qualitative and quantitatively depending on the cultivar, maturity stage, climatic conditions and the production area of the cultivar.\textsuperscript{32}

### 1.2.3.4 Other Matter

Plums contain some other constituents of nutritional importance such as proteins, vitamins, minerals, dietary fibre and organic acids. Willis\textsuperscript{12} reported the composition of plum per 100g of the edible portion with 0.6g protein, 1.56g malic acid, 0.03g oxalic acid, 4mg of Vitamin C. Malic and quinic were the major organic acids reported by Belitz and Grosch.\textsuperscript{10} These authors also reported 0.2-1.4\% of phenolic compounds in
plums. Anthocyanins also have been reported in plums.\textsuperscript{10, 26, 33-35} Anthocyanins are a group of reddish to violet water-soluble pigments, which are responsible for decolourisation.\textsuperscript{36}

\section*{1.3 THE PRODUCTION OF DRIED PRUNES}

The production of dried prunes relies on several food processing operations. The desire to establish and maintain the economics, stability and quality of the product necessitates better understanding of the operations involved in the production. A typical processing concept involved in the commercial production of prunes is illustrated in Figure 1.3.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{production_diagram}
\caption{Typical processing concept for the production of prunes.}
\end{figure}

The schematic diagram describes the major steps needed in the manufacturing of dried prunes. Fresh plums are washed and cleaned, and graded according to different sizes. During this step undesirable fruit are also eliminated. Grading is necessary primarily because of the market demands but also the drying characteristics depend greatly with the size of the fruit. Immediately after grading, the fruit are placed in trucks on trays according to size ready for drying. Following grading, the high-moisture fruit are dried down to a moisture content desirable for long-term storage. As will be explained later,
this step is considered important as it greatly affects the production efficiency and product quality. Dried product is then placed in bulk storage usually in large wooden bins until subsequent processing. If properly dried, the prunes can be stored for long periods of time at ambient conditions. The fruit are subsequently rehydrated to final moisture content of about 30-35% and packaged for market. Rehydration is usually accomplished by exposing the dried fruit in hot water for about 45 minutes.

The production of prunes usually involves drying of high-moisture plums down to about 18-24% (dry basis) moisture content. A number of plum varieties are used for drying including Ente and d'Agen. These cultivars are distinguished by their high solids content (about 25-30%). In many countries other varieties such as Robe de Sergeant, Imperial and Sugar are also utilised for drying. The process of drying fresh plums as a large scale is practiced in many countries. A number of countries still use sun drying. Sun drying has been for centuries the method employed for the production of dried products. The time consuming process, the danger of contamination and spoilage due to the exposure to environmental condition and the dependence on the weather have made this method obsolete. Improved drying techniques have widely replaced solar drying in the search for economically efficient process and better quality product. Today, nearly all prunes are mechanically dehydrated. This is normally carried out in long dehydration tunnels with typically high airflow (about 5 m/s) using gas burners.

Tunnel dehydrators are widely used in the commercial dehydration of fruits. In tunnel drying the plums are moved at regular intervals on a continuous basis through the drier. This means that the fruit are exposed to varying conditions during drying. The tunnel dehydrators are operated either in counter-flow or parallel-flow manner (Figure 1.4). In counter-flow configuration the drying air is introduced into one end of the tunnel while the trolleys of fruit enter at the other end and moved in the opposite direction. This type of dehydration is characterised by having conditions most conducive to rapid heating at the end of the cycle when the prunes are nearly dry and slow drying at the early stages. McBean et al suggested that the maximum temperature to which the prunes are exposed as they approached the outlet end should be about 71°C. These authors observed that the relative humidity at the hot end was about 17-25% and about 45% at the cooler end where the fresh fruit enter. Mrak and Perry recommended that for
prunes dried in a counter-flow fashion, the air at the cooler end where fresh fruit enter should have a humidity of 65%.

![Diagram of commercial prune tunnel dehydrators](image)

**Figure 1.4.** Schematic diagram of the commercial prune tunnel dehydrators.

The operation of a parallel-flow tunnel is opposite to that of counter-flow. The trolleys of fruit and the drying air enter into the same end of the tunnel and progress through the dehydrator in the same direction. This method of drying is described by rapid removal in the early stages where the product to be dried is still very wet followed by slower drying as the fruit approach the cooler outlet end. Gentry et al\(^43\) found that with the parallel-flow inlet air temperatures of up to 90°C could be employed without heat damage to the prunes due to evaporative cooling effects.

In many respects the differences between the two methods of drying plums are significant. McBean et al\(^41\) demonstrated that parallel-flow drying offered advantages of shorter drying time than counter-flow without loss in quality of the product. They carried out the comparison of the two methods in both laboratory and commercial scale and found an almost half reduction in total drying from 27 hours in counter-flow with temperature of 54.4 to 71.1°C and humidity of 28 to 10% to just around 15 hours in
parallel-flow with temperature of 90.5 to 71.1°C and humidity of 10 to 27%. Gentry et al\textsuperscript{43} indicated that the throughput of prunes could be increased by 30-40\% in employing a parallel-flow method of drying. They also observed that fruit quality in relation to the methods of dehydration showed no important differences for prunes dried to 18-20\% (dry basis) moisture content. However, these authors stressed that caramelisation which is undesirable in dried prunes may be more of a problem in counter-flow than under parallel-flow drying since high air temperatures occur in the former when the sugar concentration is high. Over-drying of prunes is also considered highly undesirable because not only does it impair fruit quality but also it reduces the dehydrator output.\textsuperscript{43}

In the production of prunes, it has been previous commercial practice to dip fresh plums with hot caustic soda solution (about 0.2\% NaOH) to enhance drying.\textsuperscript{38} According to this author the treatment has the tendency to cause slight cracking or checking of the skin and is believed to remove some of the waxy bloom on the surface of the skin. The practice of dipping prior to drying however has been ceased partly because of concern over product quality. Other industries such as the sultana industry have used fatty-acid emulsions\textsuperscript{44, 45} to enhance the dehydration. Some researches have been carried out to see if plums would benefit from this\textsuperscript{46, 47}, but it is still unclear as to how effective they are, and under what conditions they are optimal. This has reawakened an interest of looking at the effect of dipping pretreatment on the drying process of plums.

1.4 THE DRYING PROCESS

1.4.1 Water in Foodstuffs

Water is a major component of most foodstuffs and plays an important part in processing and production. It is the self-association of water molecules and their attachment with other compounds that provides the structural basis for foods.\textsuperscript{48} Water content of foods varies widely. In plums, for example, it accounts for about 70-85\% (wet basis) depending upon cultivars and climatic conditions at harvest. The water content of foods exerts a profound influence on their physical properties and processing behaviour.
Moisture content has an important role to play in drying technology. In solid materials, it is usually inferred from a loss in mass on drying. The amount of moisture present in foodstuffs is conventionally expressed in terms of wet and dry basis often as a percentage. Moisture content in terms of dry-basis is simply the mass ratio of the amount of moisture to bone-dry matter of the solid whilst the wet-basis moisture content is the percentage of moisture to the wet-weight of the sample. There is a wide range of techniques available for measuring the amount of moisture present in the material. This includes conventional drying, forced-air ovens, vacuum ovens, microwave ovens, chemical and physical methods. The most common approach is gravimetric. This involves drying a pre-weighed sample to a constant mass under carefully controlled conditions. Vacuum ovens are usually employed to hasten the process whilst minimising exposure to high temperatures. Standard procedure adopting this method for moisture analysis of various foods has been established by AOAC. Today, this remains the standard method for the determination of the total moisture content of many foods.

It is important to understand the behaviour of water in the foods to be dried so that it can be extracted most efficiently without affecting the quality of the product. It has been recognised that the water in foods exists both in bound and free forms. Water content in the food may be also present in vapour form mixes with air, which occupies the empty spaces unsaturated with free water. The state of water in foods is of importance to drying as free water is relatively easy to remove from a food product while bound water takes more energy to release from the food. The free water fills the largest part of the cavities of the structure, which is trapped in a liquid state by capillary forces. Often the thermodynamic measure of the water activity is used to describe the water interactions in food products. Water activity ($a_w$) is defined as the ratio of the vapour pressure of water measured at the food surface to the saturation vapor pressure of pure water at the same temperature. It is also thought to be related to the availability of water molecules to enter into reactions. For instance, a water activity of 1 is denoted to free water while the bound water is that which gives water activity less than 1. If $a_w$ is high water molecules are free to react both as solvent or reactant whilst a low $a_w$ implies that the water is more tightly bound and less able to react. The relationship between water activity and moisture content has been studied for various foods, including dried prunes.
It is also a common observation that foods with high moisture content are more susceptible to rapid deterioration due to biological and chemical reactions. The influence of moisture content has also obvious effects on texture. Water content influences the storability and susceptibility of the product to microbial spoilage. Microbial spoilage has an enormous effect on product quality and is dependent on the amount of moisture present in the product. It has been recognised that for many foodstuffs there is optimum moisture content and a corresponding water activity at which maximum stability can be achieved. In fact, moisture content has become an important product quality measure in the food processing industry and has been used as marketing standard.

1.4.2 Drying Mechanisms

Drying encompasses simultaneous heat and mass transfer processes. There is a great deal of literature regarding the theoretical fundamentals of drying (e.g. Strumillo and Kudra, Toei, Van Arsdel and Keey). Chirife and Achanta and Okos give comprehensive reviews of the theory of drying foods. Air-drying is the most common method for drying foodstuffs. In air drying, heat is transferred from the drying air to the product in which the energy transmitted to the product activates the water molecules. This induces the movement of the water molecules from the product into the drying air. The movement of water during drying is a complex process, which involves diffusion within the food matrix and evaporation into the drying air. Water molecules must negotiate their way through the product to the surface in contact with the drying air. During drying water moves from points within the product to nearer the surface. This creates a redistribution of moisture within the food matrix. A state of higher moisture content at the center and lower at the surface is usually attained. As a result diffusion of moisture occurs due to concentration gradients being established.

Fruits like plums are known to be covered by a waxy skin layer having properties different from those of the underlying tissue. In the course of drying this type of fruit, internal water transport may occur by means of two different resistances. This means that water must migrate from the interior of the fruit to the skin and diffuse through the skin layer. The resistance offered by the skin layer for moisture transport could therefore
mainly control water loss. The internal movement of water molecules within the fruit matrix is a fundamentally diffusion-like mechanism, which is driven by concentration gradient. Once at the surface of the product, water evaporates into the drying air, which is eventually carried away from the product. The external mass transfer is driven by the difference between the vapour pressure of water at the surface of the product and the air.63

Consequently, the kinetics of drying may be governed by either the rate of water diffusion to the surface or the rate of evaporation from the surface into the drying air. In fact, most foods of high-moisture content exhibit an externally controlled drying during the initial stages followed by an internally limited drying process as the product dries out. The extent of these processes is usually identified by the behaviour of the rate of moisture loss. Initially, the rate of drying may be constant until a critical moisture content is attained. This initial phase of drying is usually referred to as the constant rate period. The next phase known as the falling rate period follows when the amount of water in the product falls below critical moisture content. The typical drying behaviour is illustrated in Figure 1.5. Several researchers have observed this behaviour particularly during drying of high moisture fruits and vegetables. For example, Lopez et al64 observed two distinct periods (constant & falling rates) during drying of onions at temperatures of 60-80°C. Saravacos and Charm65 studied the drying of fruits and vegetables and observed the presence of both periods of drying in most products.

In the constant-rate period, the drying process is limited by the rate at which water molecules evaporate from the product surface into the drying air. In this case, the moisture content at the surface of the product is considered to be constant, as the water replenishment from the interior to the surface is sufficiently rapid to maintain a constant surface condition.54 This means that the rate of water migration from the interior to the surface is greater (or equal) to the rate at which water molecules are transferred from the surface to the drying air. In constant-rate drying, material structure has no influence and is mainly dependent on the properties of the drying air.66 This period extends so long as the surface of the product is fed with free water from the interior so that the moisture content at the surface is constant. Once the moisture diffusion from the interior is slower
than the surface evaporation the constant-rate period ceases to exist. The average moisture content of the product at this point is termed as the critical moisture content.

![Diagram](image_url)

**Figure 1.5.** Typical drying rate curve for a food product (adapted from Heldman and Hartel\textsuperscript{54}).

The falling-rate period sets in once the critical moisture content is reached and the rate of moisture diffusion from the interior to the surface limits the drying. Thus the rate at which the moisture is replenished at the surface is slower than the rate of moisture evaporation from the surface to the drying air. The process of internal mass transfer often involves different mechanisms of moisture movement.\textsuperscript{59} According to Heldman and Hartel\textsuperscript{54}, the moisture within the food product can migrate in several ways via a number of different mechanisms. That is the water diffuses through the product in a liquid or vapour phase.\textsuperscript{66} In liquid diffusion, the rate at which moisture migrates depends on the nature of the food product, temperature and the concentration difference between the surface and bulk\textsuperscript{54}. In some cases, vaporisation may occur within the product and water diffuses in the form of vapour through the food matrix to the drying air with the difference in vapour pressure as the driving force. During drying other mechanisms of moisture flow may also apply. Surface tension forces (capillary flow),
the differences in pressure between the drying air and the internal food structure (pressure flow), and the differences in the temperature between the surface and the interior of the product (thermal flow) may influence the mobility of moisture.\textsuperscript{56} According to Brennan et al\textsuperscript{67} liquid diffusion and capillarity have received the most detailed treatment. If drying continues, there is a point in which the product eventually equilibrates with the drying air, which signifies the end of drying. Equilibrium moisture content is a steady-state condition obtained by a material exposed to specific drying conditions. The equilibrium point usually depends on temperature and relative humidity of the drying air.

The temperature profile of the product during drying may be used in identifying the different periods of drying. Initially, the energy supplied by the drying air is utilised for heating the product up to a certain temperature level. Further heating eventually causes the water molecules to be released from the product surface into the drying air. During the constant-rate period, all the heat transmitted from the drying air to the product is consumed in the evaporation of moisture.\textsuperscript{57} Thus, the product temperature remains constant until such time that all the moisture at the surface has been depleted. In a real system, heat may be transported from the drying air to the product surface by convection, conduction or radiation.\textsuperscript{68} Heat reaching the surface is transferred generally to the interior by conduction. Upon arriving at the interface, heat is available to activate the water molecule and transport it through the solid to the surface. However, in the common case of air drying, convection is the predominating mechanism.\textsuperscript{48} If drying occurs only by convection, the temperature of the product during the constant period stabilises at the wet bulb temperature of the drying air. If other heat transfer mechanisms are involved a slightly higher temperature is attained.\textsuperscript{67} Once the moisture contents at the surface have been exhausted (which signifies the start of falling-rate period), the product temperature rises in a characteristic fashion. This is because the amount of heat used for heating up the material increases since the amount of heat required for vaporisation of moisture at the surface decreases. This trend continues until the product temperature eventually approaches that of the temperature of the drying air. It should also be recognised that the product temperature profile is important, as most quality attributes of food products are dependent on temperature.
There are many factors that influence the kinetics of moisture transport during drying. These include both properties of the air together with characteristics of the product itself. Perhaps the process conditions such as temperature, velocity and relative humidity of the drying air represent the major factors controlling the rate of drying.

It is widely recognised that the drying process is accelerated at elevated air temperatures. The actual temperature of the drying air is important because it determines the maximum amount of water vapour that the air can hold. Elevated temperature would mean an increase in the rate of drying due to greater rate heat transfer which eventually results in higher rate of vaporisation. Also, if the temperature increases the relative humidity of air at given moisture content falls. This enhances the drying potential as a consequence of higher driving force for mass transfer from the product surface. Higher temperatures also mean that there is greater energy available for the activation of water molecules within the food matrix. Obviously, this causes the water molecules to migrate more rapidly and subsequently increases the internal rate of drying. According to Heldman and Hartel, elevated temperature improves drying by affecting both internal (falling-rate period) and external (constant-rate period) mechanisms of moisture transport. In food products, however, caution is needed as extreme temperatures may alter the physical and chemical compositions of the food product, which affect the quality. Increases in temperature also mean an increase in energy consumption. Thus it is important to determine the practical temperature limit at which the food product can be dried.

Air is never absolutely dry. It usually contains some degree of water vapour or moisture. The relative humidity of the drying air is also known to affect the rate of drying. It denotes the amount of water vapour actually present in the air. Relative humidity is related to the ratio of the actual vapour pressure in the air-water mixture with respect to the saturation vapour pressure of the moisture at the same temperature. This means that when the relative humidity is 100% the air is fully saturated with water vapour and consequently is a powerless drying agent. Generally, its main influence is only limited to the constant-rate period of drying and has little effect on drying in the
Chapter I

falling-rate period. Lowering the relative humidity of the drying air enhances drying during a constant-rate period. This is due to the increased difference in moisture vapour pressure between the product surface and the drying air, which represents the driving force for external mass transfer. It should be noted that the relative humidity of the drying air also determines the equilibrium moisture between the air and the product at which the drying process ceases.

The velocity at which drying air passes across the product surface also influences the kinetics of drying. Effect of the drying air velocity mainly impacts on the rate of external moisture transfer. It has normally little effect on drying during a falling-rate period, which is an internally controlled process. Air is required to transfer heat and to remove the moisture away from the product. Increased air movement over the product enhances the evaporation rate as a result of improved convective mass and heat transfer rates. This consequently shortens the constant-rate period of drying. Regulation of air movement during drying is therefore of great importance particularly during the early stages of drying when external mass transfer predominates.

Many researchers have investigated the effect of process parameters on the drying kinetics of various foodstuffs. For instance, Mulet et al. studied the effect of air velocity on carrot drying and found the presence of critical velocity values above which it becomes negligible. In air drying of potato cylinders, McMinn and Magee observed significant influence of temperature and a limited effect of air velocity on the drying rate. Vagenas and Marinos-Kouris investigated the effect of temperature and velocity on the kinetics of apricot dehydration and observed a significant influence of both parameters. There has been relatively little work on the factors affecting the drying kinetics of prunes. Perhaps the most significant ones have been the investigations by Barbanti et al. and Bousigon et al. These authors have shown the influence of some process parameters (i.e., temperature and velocity) upon the drying kinetics. More recently, Newman et al. studied the effect of drying air temperature (70-100°C) on the drying kinetics of d'Agen plums. This was only a preliminary study, however, they observed significant differences in drying rates between temperatures. Other conditions of the drying air such as velocity and relative humidity were not either reported or
monitored. In addition, the total drying time in which the final moisture content conforms to that of desirable in commercial level (about 20%) was not reported. In particular, no studies have focused on the effect of the drying air relative humidity on the kinetics of drying prunes.

In order to optimise the process in terms of efficiency and product quality and to predict the course and extent of the changes under different drying conditions, realistic models which describe the phenomena taking place during drying are needed. Mathematical modelling is now widely used to describe the drying process of various foodstuffs. There are several proposed mathematical models to predict the mass transfer process during drying of foodstuffs. Parry\(^7^6\) reviewed different mathematical models applied to grain drying. Many articles have also been published recently concerning the modelling of fruits and vegetables in particular.\(^7^7^\text{-}^8^0\) The vast volume of literature published annually on modeling of drying of various materials exemplifies the extreme diversity of the drying mechanism. There is no universally accepted drying model because of the complex and heterogeneous structure of foods and the physical and chemical changes that may take place during drying.

1.5 EFFECTS OF DRYING ON PRODUCT QUALITY

Flavour and aroma of foods are important quality factors that influence the value of the product to the consumer. Transformation of foods by processing into a stable product driven by the need for high value-added product has always quality consequences. The ultimate aim of processing is to minimise product quality changes while optimising process efficiency and minimising costs. There are several chemical degradation reactions that may occur during drying that influence the quality of the product. One of the main problems associated with drying is the loss in flavour and nutritive value due to thermal degradation of the food constituents. Identification and understanding the extent of these reactions would provide means of optimising the drying parameters in relation to product quality.
1.5.1 Thermal Degradation of Carbohydrates

Carbohydrates are the most abundant class of organic compounds found in living matter. In plants, they constitute more than 90% of dry matter. The process of photosynthesis in which carbon dioxide and water are synthesized in the presence of light energy achieves the formation of carbohydrates in green plants. In fruits, there are four major simple carbohydrates that can be found. These are glucose, fructose, sucrose and sorbitol. Both glucose and fructose are classified as monosaccharides. They are also called reducing sugars because they contain a free aldehyde or ketone group, which act as reducing agents. Monosaccharides are carbohydrate molecules that cannot be broken down to simpler molecules by hydrolysis. Glucose, which is usually referred to as grape sugar, is a major product of photosynthesis. It is the most abundant monosaccharide that is widely found in foods and is occurring naturally in fruits. Glucose is an aldohexose, which means it is a carbohydrate containing aldehyde group with six carbon atoms. In plants, glucose is also found by hydrolysis of starches. On the other hand, fructose, which is commonly referred to as fruit sugar, also occurs in abundance in many fruits. It is a ketohexose indicating the presence of ketone group. Sucrose is also amongst the sugars found in plants, which plays significant role in food processing. Unlike glucose and fructose, it is a disaccharide composed of two monosaccharides (D-glucose and D-fructose). It is also known as a non-reducing sugar and can easily be spliced by hydrolysis. Sorbitol (D-glucitol) known as sugar alcohol is another naturally occurring carbohydrate present in many fruits, vegetables and cereals. It belongs to the general carbohydrate group called alditols and is generally stable to heat. An important contribution of a sugar alcohol like sorbitol is its humectant properties, which is the ability to control the moisture level during storage. The chemical structures of the sugars and sugar alcohol discussed above are shown in Figure 1.6.

Analysis of carbohydrates in fruits is usually performed by chromatographic methods. High-performance liquid chromatography (HPLC) is the most common method used for this analysis. A wide variety of columns commercially available may be used for HPLC with amino-bonded silica operating at around ambient temperature has become the most popular. The amino-bonded silica columns used an acetonitrile-water mobile phase and separate mainly by partition between the acetonitrile-rich mobile phase and the water-
enriched stationary phase. Differential refractometer is the most utilised means of detection, which uses the changes in refractive index. An electronic integrator connected to the system records the output. Using HPLC method, Forni et al\(^9\) succeeded in separating sugars and sorbitol contents of 13 plum cultivars. They compared two chromatographic systems and found that the amino-bonded silica phase (LiChrosorb-NH\(_2\)) yielded a better resolution and sensitivity compared to the polymeric phase (Polypore Pb). Wilford\(^{14}\) also successfully analysed the carbohydrate contents of d’Agen plums using an HPLC method.

The great interest in monitoring thermal degradation of carbohydrates during drying of food stems from the desire to control the quality of the dried product. Most carbohydrates are susceptible to heat treatment. Many of these changes are due to combined effects of other conditions. Perhaps the most important chemical reactions during drying, which have a decisive influence on the quality of the dried product, include acid hydrolysis, Maillard and caramelisation. These reactions may proceed simultaneously. The course and rate of these reactions are primarily influenced by
chemical composition, acidity, temperature and moisture content. Depending on the conditions, the extent of these reactions varied considerably.

The hydrolysis of the glycosidic bond of sucrose to glucose and fructose can be catalysed by acid or enzymes. Breakdown of sucrose is usually referred to as inversion because the optical rotation of the solution changes from right to left during the reaction. The products of sucrose hydrolysis i.e. glucose and fructose are relatively stable in mildly acidic and neutral solutions. Monosaccharides were reported to be stable in mildly acidic solution of pH range of 3-7. Shallenberger reported that fructose is most stable at pH 3.3 while glucose has an optimum stability at pH 4. With the presence of amino compounds, monosaccharides may undergo further reactions particularly in strong acids, or alkaline solutions of high temperature.

Maillard (also known as non-enzymatic browning) is the most important reaction of carbohydrates with other food constituents. It involves a complex chain of reactions, which lead to the formation of insoluble brown polymers called melanoidins. Maillard reactions occur widely during heating or prolonged storage of foods. In food systems, it normally occurs between the reducing sugars and nitrogenous compounds in particular amino acids and proteins. It plays a significant role in the food processing as it leads not only to the formation of colours and flavours but also to the destruction of some food constituents with nutritional value. This results in the deterioration of food quality by reducing the availability of amino acids and proteins.83

There are several indicators of Maillard reaction that can be used for quality control. These include the production of color, flavour, water and carbon dioxide. Lowering the pH, loss of vitamin C and proteins are also important indicators. Perhaps the most significance to the food industry are the discoloration, production of off-flavours and the reduction in nutritional value. During storage the increase in $a_w$ because of the production of water may be also important. With the knowledge of Maillard reaction, the operation of drying should therefore be expedited as much as possible without causing intolerable degree of degradation. The detection of Maillard reaction should provide additional information on the quality control during processing and storage.
Caramelisation is another important reaction involving thermal degradation of sugars. It is a complex reaction of heating sugars in the absence of nitrogenous compounds leading to the formation of dehydration products, pyrolysis products, and polymers and coloured substances. Sugar degradation reactions are characterised by initial enolisation, followed by dehydration, dicarboxylic cleaving, retro-aldol reaction, aldol condensation and finally a radical reaction. These reactions give rise to aliphatic sugar degradation products, which can react further to produce oxygen heterocyclic and carbocyclic compounds via aldol condensation. The key intermediates of the thermal caramelisation are $\alpha$-dicarbonyl compounds such as 3-deoxyhexosulose. These lead to the formation of caramel colour and give rise to important volatile products typical for caramel flavour. The caramelisation reaction, which is directed towards the formation of aroma and brown pigment accumulation, could therefore be used as a quality control indicator.

### 1.5.2 Volatile Formation during Drying

Fruits consist of a complex assembly of chemical compounds that are responsible for their odoriferous characteristics. These volatile compounds are reminiscent to their unique natural aromas. It is recognised that the consumption of fruit is highly motivated by its desirable aroma and flavour. Aroma and flavour have been the subject of a large number of studies over many years. Volatile constituents of many fruits are known to exist as extremely complex chemical mixtures. This requires sophisticated analytical tools for their separation and subsequent identification. The volatile components are typically determined using capillary gas chromatography (CGC), gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) or gas chromatography-Fourier transform infrared spectroscopy (GC-FTIR). Great progress has continued to be made in this area over the last decades. At present, gas chromatography coupled to mass spectrometry is the most routinely used technique for the analysis of volatile constituents in foods.

Isolation of volatile compounds is the most crucial step in the evaluation of aroma quality. Many studies have clearly demonstrated that the constituents of the extracts are
dependent on the isolation procedures employed. These include the way in which the volatile constituents are extracted and introduced onto the column of a GC-MS system. Several extraction techniques have been studied for food analysis. Conventional methods include solvent extraction, vacuum distillation and simultaneous steam distillation-extraction. However, large amounts of raw materials and lengthy procedure are required for these methods. Another technique is to extract the volatile constituents in the headspace above the material with a purge-and-trap either cryogenically or on a solid phase absorbent. Headspace analysis provides a volatile profile similar to the aroma perceived by smelling. Most recently, the capability to elucidate chemical composition of substances within the complex mixtures in small quantities of sample has improved further through innovations such as solid-phase microextraction (SPME). This solvent-free technique is based on adsorption of analytes on a phase-coated silica fibre. The adsorbed compounds to the fibre are thermally desorbed onto the injection port of the GC-MS system. SPME has been successfully applied to the analysis of volatile flavour in foods and beverages.89, 90 The development of micro-technique for monitoring volatile flavour formation as an indicator during drying appears to have great potential for quality control.

Many chemical degradation reactions are known to occur when foods containing carbohydrates and amino acids or proteins are thermally processed. These reactions which may involve degradation of sugars alone or in combination with amino acids are important routes for the formation of a wide variety of end products including volatile aromas. Food of various constituents when subjected to heating often results in a wide spectrum of aromas. Most of these volatile compounds are from the commonly occurring degradation reactions such as Maillard and caramelisation. The important volatile constituents include hydrocarbons, aldehydes, ketones, alcohols, esters, acetals, carboxylic acids, lactones and heterocyclic compounds.36 Nursten91 classified the volatile formation of these reactions into three categories which include from sugar degradation (furans, pyrones, cyclopentenes, carbonyl compounds and acids), amino acid degradation (aldehydes and sulfur compounds), and volatiles produced from further interactions which produce heterocyclic compounds. The important heterocyclic compounds of thermal aromas include pyrazines, pyrroles, pyradines, oxazoles and thiazoles.92 Pyrazines, which are widely found in heated foods, are formed by the
Maillard reaction and by pyrolysis of some amino compounds. Volatile aromas formed from this complex chemical transformation may be used in turn as quality control markers.

Several studies looking at the volatile flavour variation of prunes as influenced by processing have been reported. Among these studies were summarised by Crouzet et al. For instance, Ismael et al when comparing canned and fresh plums found that after processing, the major headspace constituents were shown to be benzaldehyde, 2-furaldehyde, 2-furylmethyl ketone and nonanal, with pentane-2,3-dione, 3-hydroxybutanone, carvone and acetophenone as minor constituents. As reported by Crouzet et al, dried prunes contain less ketones, aliphatic aldehydes and alcohols, hydrocarbons and esters than the fresh plums. These authors also observed a difference before and after heating of plums, which showed that the concentration of benzaldehyde increased significantly. Ismael studied the aroma of canned plums and found benzaldehyde and nonanal as the major constituents. 2-Furaldehyde was also identified in the headspace as one of the major constituents. This author suggested that the three major volatile compounds probably arose from thermal treatment of the fruit, either by activation of enzymatic degradation of precursors at the first stage of heating or by chemical degradation of sugars and amino acids. It was further mentioned that the difference in aroma between canned plums and jam could be due to the difference of duration and intensity of heating applied to the fruit in both processes. Furfural (2-furaldehyde) was also found in large quantities of brandies which arises from the heating process. They also noticed that the mixture of damascenone, ethyl cinnamate and γ-lactones, which are natural constituents of dried plums, produces odours reminiscent of the aroma of cooked plums. Among other important volatiles found in cooked plums are ketones. The process of drying applied to foods may also induce formation of new aromatic compounds. It is known that sugars and amino acids are degraded in several mechanisms by heating yielding a number of volatile compounds. Crouzet et al pointed out that some clues of the sugar degradation reactions can be observed as furfural, methylfurfural, acetylfuran and furfuryl alcohols were identified in dried prunes. In order to confirm the occurrence of Maillard reactions, Moutounet and Jouret followed the decrease in amino acid content in plums during heating and found
a decrease of 75-80%. These studies exemplified the importance of volatile flavours to the product quality. However, there is very little information on the volatile formation during drying under different conditions. In addition, no studies can be found on monitoring the changes in volatiles during drying.

Flavour compounds that are typically more volatile than water are removed during drying process. The physical forces that cause removal of water molecules from the food during drying may also cause the removal of the volatile flavour constituents of foods. Water is not the only volatile component that will escape from the food during drying. As a result the original aroma characteristics of the product may be diminished because of drying and affect the quality. Thus the dried product usually has less or different volatile flavours from its original form. In addition, the rates of chemical degradations are enhanced at higher temperatures and many of these reactions generate new volatile flavour compounds. The magnitude of these reactions during drying depends to a great extent on the nature of the drying process. Monitoring the volatile flavour formation associated with the chemical degradation reactions may further enhance our understanding of the drying process. This may serve as guide in identifying the degradation reactions that are occurring during drying. It has also a great implication as an indicator of the degradation reactions, which could be used for quality control.

1.6 AIMS OF THIS RESEARCH

The main objective of this research was to establish a scientific basis for suggesting improvements to the commercial production of prunes. In order to achieve this, it is important to understand the underlying mechanisms of physical and chemical changes occurring during drying. A computer-controlled drying system was developed to study the physico-chemical aspects of drying plums under controlled conditions.

Transport phenomena of moisture in foods during drying are usually complex involving several mechanisms. It was the first task to ascertain the major factors controlling the rate of drying and elucidate the drying mechanism. This highlighted the effects of process parameters (i.e., drying air temperature, velocity and relative humidity) on the kinetics of moisture transport during drying. In order to further examine the rate-
controlling mechanisms involved during drying, ancillary experiments were conducted looking at the rate in which moistures are able to diffuse across the skin layer by using a radiotracer technique. Using the above information, physical models capable of describing the kinetics of drying plums under a wide range of drying conditions were formulated to further explain the mechanisms of moisture transfer during drying. This work presented the validation of the proposed models against the experimental data and their relevance to interpreting the rate-controlling mechanisms involved during drying of plums.

The successful use of drying emulsions based on fatty acid esters particularly in the sultana industry makes it attractive to the production of prunes. It was therefore thought worthwhile investigating its applicability to the drying process of plums. This is also important to further augment the role of the skin layer during drying as the pretreatment is mainly intended to disrupt the skin layer. In this context, the effect of various drying emulsions, as a treatment prior to drying, on enhancing the rate of moisture loss during drying was explored. The focus was to further exploit the applicability of a commercially available drying emulsion by looking at its effectiveness under different drying conditions. A number of ancillary techniques were used to evaluate the mode of action of this chemical pretreatment including an examination of its effect on water permeability of the skin. Pilot testing at a commercial level was carried out to investigate the feasibility of incorporating the chemical pretreatment procedure under current prune drying practices and to assess the chemical residues in the processing equipment and the products.

Monitoring the changes in the chemical constituents of plums during drying and storage was the next task as there may be important chemical degradation reactions occurring during this period which could be of interest for the control of product quality. To evaluate the occurrence of the degradation reactions, the kinetics of carbohydrate change in plums during drying were followed by using standard HPLC technique. In an attempt to assess the major factors affecting the degradation reactions, the effects of the drying conditions and the pH of the fruit on the kinetics of carbohydrate change were studied. Changes in the carbohydrate contents of dried products during prolonged ambient storage were monitored to study the degradations occurring during this period. Likewise,
it is known that the decomposition of carbohydrates may lead to the formation of wide variety of volatile flavours. The approach of aroma profiling was then examined to establish further avenues of detecting the progress of chemical degradations associated with drying. This addressed the development of a micro-technique suitable for the analysis of headspace volatile components from a small quantity of sample. It examined the applicability of SPME technique in conjunction with GC-MS for flavour profiling during drying of plums. This was carried out in an effort to identify the volatile flavours associated with the chemical reactions involved during thermal degradation of carbohydrates.

The importance of controlling the conditions during drying prompted us to develop a computer-controlled data acquisition system which could be used to monitor and record the conditions of the drying air as a function of time and position during commercial drying of prunes. The rationale of the work was to gain better information of the conditions during commercial drying to use in conjunction with the laboratory-scale studies. It was also the intention to demonstrate the utility of the monitoring system in evaluating the performance and efficiency of the tunnel. This covered the design, development and testing of a simple automated device for on-line monitoring of the drying conditions.
Chapter 2

THE KINETICS OF MOISTURE TRANSPORT DURING DRYING OF PLUMS
2.1 INTRODUCTION

Plums of d’Agen variety are extensively grown mainly for the production of dried prunes due to their high solid content. Presently, one of the major needs within the prune industry is to improve the processing efficiency in order to effectively compete in the global market. The processing of prunes usually involves drying of high-moisture plums and the energy costs expended during the drying process account for a major portion of the total production costs. Therefore, significant reductions of these costs are desirable.

Drying, a well-established process in the food industry, is one of the most costly operations of industrial significance. It involves mass transfer characterised by simultaneous diffusion of moisture through the food matrix and evaporation from the surface. Evaporation of moisture from the product surface is usually influenced by the process parameters including temperature, humidity and velocity of the drying air. Water movement within the food matrix results from concentration gradient, which is dependent on the characteristics of the product. The importance of drying provides a need to understand the controlling transport mechanisms in order to achieve a more efficient drying process. Understanding the factors controlling the rates of the process is of great importance in obtaining optimum drying conditions.

Though the physical moisture loss is one of the most important steps in understanding the drying mechanism, it is also meaningful to identify the associated changes within the material during the different stages of drying as these changes may affect water mobility. Some fruits have a pronounced waxy skin layer. Plum is one of this type which possesses a skin having properties different from those underlying layers. This waxy skin layer acts as an efficient barrier to moisture transport and impedes water movement from the fruit to the environment. Whilst the movement of water within the fruit matrix results mainly from a concentration gradient, its mechanism may be affected by the structural properties of the material. Understanding the structural composition of the fruit and the changes occurring during drying may further augment our knowledge of the complex nature of the drying process.
Several studies have been conducted to improve and describe the drying process of prunes. McBean et al.\textsuperscript{41} looked at a number of aspects of the drying process including design of tunnels (counter-flow versus parallel-flow) in both Australia and USA. They investigated the effect of experimental parameters on final prune quality rather than the physico-chemical basis of moisture loss process. Other research has been directed to studying the effect of waxy skin layer on the drying process.\textsuperscript{7, 8, 95, 96} However, there is very limited work using current drying practices. In recent studies, Barbanti et al.\textsuperscript{22, 23} and Bousigon et al.\textsuperscript{74} have shown the influence of some process parameters upon the drying kinetics and on the engineering design of dryers. These drying studies took place using different varieties and in a different range of operating conditions from those used here.

The aim of the present work was to investigate the major factors controlling the kinetics of moisture loss during drying of plums. This includes experiments highlighting the effect of the process parameters such as temperature, humidity and velocity of the drying air. The water permeability across the waxy skin layer and the water transport within the flesh were investigated. It was envisaged that the data generated from this work would provide information for use in devising cost-reduction measures in commercial drying of prunes.

In this work, a computer-controlled experimental dehydration system was designed and developed to study the kinetics of drying plums under controlled drying conditions. Water permeability across the skin of the plums was evaluated using a radiotracer method. These ancillary experiments were carried out to further elucidate the rate-controlling mechanism during drying of plums.

\section*{2.2 EXPERIMENTAL}

\subsection*{2.2.1 Materials}

Fresh plums of d’Agen variety were used in this study. They were obtained from the Young district of New South Wales, Australia. The fruit were sorted according to size to obtain an approximately homogeneous sample. Plums weighing between 10 to 20
grams, which represented the average size, were utilised. Samples were kept in sealed plastic bags purged with nitrogen. These were then stored in a refrigerator at 4°C (±1°C) prior to the drying experiments.

2.2.2 Preliminary Batch Drying Experiments

Preliminary batch drying experiments were conducted to investigate the drying characteristics of plums. A simple laboratory forced-air oven (Labec) was used in the study. It basically consisted of fan, resistance heater and drying chamber. Inside the oven were trays for holding the plums. The drying chamber was equipped with an automatic temperature controller. The airflow was turbulent and was always less than 0.3 m/s.

Mass loss due to drying was monitored at 1-hour intervals until the end of the drying period by taking out samples allocated for each time interval. Weighing was achieved using a Mettler P3600 electronic balance with a sensitivity of ± 0.01 g. The conditions of the drying air (temperature and humidity) were monitored by using a Vaisala HMP 233 transmitter (Vaisala, Melbourne) which had sensitivities for temperature and humidity of ± 0.1°C (in the range -40 to 120°C) and ± 1% RH absolute (in a range up to 90% RH), respectively.

Drying experiments were carried out under different conditions of drying air such as temperature and relative humidity. The drying air temperatures tested were 70, 80, 90 and 100°C. Three levels of relative humidity of the drying air were examined (i) low (<5%), (ii) medium (20-40%), and (iii) high (40-65%). These sets of conditions of relative humidity were achieved by adjusting/restricting the venting of the exhaust gases and introducing a source of moisture into the drier by way of a tray of heated water placed on the floor of the drier.

Six plum samples were allocated and removed for each time interval and the mass loss was evaluated. Samples were selected in such a way that they were taken from different sections of the oven to compensate for any small uneven temperature distributions. Dried fruit samples were then cooled at room temperature before weighing. Each drying
run was carried out past the normal moisture content of commercial products (about 18-20%, dry basis). All experiments were repeated at least twice.

### 2.2.3 Design and Development of an Improved Experimental Dehydration System

An improved laboratory-scale dehydration system was developed to investigate the kinetics of drying plums over a wide range of drying conditions. The drier was specifically designed to study the mechanism of moisture loss in controlled conditions and also to simulate conditions in a typical commercial dehydration tunnel. It allowed online monitoring and data-logging of sample mass and the experimental conditions during dehydration. The experimental setup consisted of two major components, namely; (1) the dehydration unit, and (2) the automated data acquisition system. A schematic diagram of the dehydration system is shown in Figure 2.1.

![Schematic diagram of the experimental dehydration system.](image)

**Figure 2.1.** Schematic diagram of the experimental dehydration system.

The dehydration unit consisted principally of a drying chamber equipped with heating, ventilation and humidifying systems. A stainless steel mesh tray was suspended from a
top mounted digital electronic balance inside the drying chamber. It was centrally positioned parallel to the airflow direction. The drying cavity was insulated with wool to minimise heat losses. A 2.4-kilowatt heating element was used for heating the drying air. The heating was regulated by an automatic temperature controller which had an accuracy of ± 0.1°C. A centrifugal fan coupled to a variable speed motor was used to allow variation in air velocity and to obtain approximately uniform air velocity. The flow characteristics of the drying air were examined by determining the velocity profile at different locations in the drying chamber. The hot air was drawn from the heating system and forced across the drying chamber. Different humidity levels were accomplished by adjustment of an inlet/exhaust damper in conjunction with humidification. Humidification was achieved by injecting water into a specially designed catchment in the heating system into which a portion of the heating coil was positioned. The humidity control and variation was achieved by regulating the flow and the temperature of water being injected into the system and the adjustment of the inlet/exhaust flap regulating the recirculation of hot humid air.

A computer-based data acquisition system was designed and built at the Research School of Physical Sciences and Engineering of the Australian National University (ANU) in collaboration with the University of Wollongong. It consisted of a Personal Computer (486 DX) equipped with an I/O card and the necessary interfaces and sensors. In addition, the PC was equipped with an RS485 serial card, a watchdog timer and temperature monitor function (Industrial Computer Source WDT1000-P). The author carried out further modifications particularly on software development to facilitate data handling, manipulation and display.

A VAISALA HMP 233 transmitter (Vaisala, Melbourne) was used to measure the temperature and relative humidity of the drying air. The transmitter basically composed of a HUMICAP sensor and a metal box, which houses the electrical circuits. The sensor was connected to the transmitter box with 5-metre cable. In this setup, three transmitters connected in series were used to monitor the inlet, outlet and ambient conditions during the experiments, respectively. The probes were then interfaced to the computer via a RS485 serial port. The factory calibrated Vaisala probes had a quoted temperature accuracy of ± 0.1°C (in the range of -40 to 120°C) and relative humidity precision of
±1% (in the range of 0-90%). The accuracy of these probes was checked regularly to ensure that it met its specifications. The humidity calibration of the sensors was performed in stable conditions using saturated salt solutions of known humidities as a reference. This was repeated over a wide range of humidity conditions. Temperature readings obtained from the sensors were also checked against a thermocouple. The thermocouple was calibrated at standard known conditions such as the temperature of a mixture of crushed ice and water (defined as 0°C) and the temperature of boiling water at 760 mm Hg of pressure (defined as 100°C). The results from the periodic calibrations showed that the sensors remained within their quoted specifications throughout the work.

The weighing was also automatically performed with a Mettler BB2440 balance (resolution ± 0.01 g) connected to the RS232 port in the computer. This enabled continuous monitoring of sample mass throughout the drying period without removing any plums from the drying chamber. Three mass readings in each sampling time were taken and averaged to eliminate the effect of excessive noise. For each recorded mass, the effect of airflow draft through the sample was corrected by calibrating with the mass in still air and under flowing conditions. The calibration was carried out for the entire applicable mass range.

Automation of the data acquisition process was performed by a computer program written in Turbo Pascal version 7.0 (Borland International, USA) using Turbo Power Utilities Async Professional communication units. A simple windowing scheme in graphics mode was used to present the user with a status line, prompt line, data field and graphics window on screen. The main program comprised the initialisation of the serial ports (RS232 and RS485) and the watchdog timer. Then followed by some parameter initialisation including filename, sampling interval and drying parameter settings. An Event Handler which is the heart of the software was then repeatedly executed. When action is required, the program initiated that action before proceeding with the Event Handler. The actions include checking the data sampling time and responding the status of the keyboard if there is any entry. Timing was based on the PC's clock. The execution of the Event Handler involved transmitting of the data from the weighing balance and sensors and recording to an output file on PC's hard disk for later retrieval.
The data were stored in an array as ASCII text file format with tab cell separators (Excel Format). The real-time data were then numerically displayed on screen in the data window together with other parameters (i.e. current time, disk size, elapsed time, etc.). The mass loss, temperature and humidity values were also graphically plotted on screen in the graphics window to show the real-time trend.

![Flow chart of the automated data collection process.](image)

**Figure 2.2.** Flow chart of the automated data collection process.

The software was a stand-alone program (an executable program in DOS prompt) and could be included in the boot file in order to run automatically after booting up of the
computer. This was necessary because the watch dog will reset the hardware if the program does not make an appointment to reset the watch dog hardware timer. This arrangement facilitated automatic restarting of the data logging process following the hardware reset without operator intervention. At startup, the program checked the command line for specific entry of some parameters. If no entry was made after the set time, then default values were assumed and data logging proceeds. The data logging process could be continuous or set to stop. The logging intervals were variable. The flow chart of the data collection process is shown in Figure 2.2. The program listing is presented on disk as a text file.

2.2.4 Instrumentation

2.2.4.1 Measurement of Fruit Temperature Profiles during Drying

The fruit surface and centre temperatures were monitored with time by using two iron-constantan thermocouples with a diameter of 0.5mm inserted into the sample, one into the flesh adjacent to the stone and the other as close to the fruit surface as possible without exposing the thermocouple. The cold junction used was ice (0°C) and the resultant potential difference was measured using a six figure digital multimeter (Hewlett Packard 3468 A) and converted to temperature using standard tables. The estimated deviations of the measured fruit temperature profile for two replications were in the range of 0.1-1.5°C.

2.2.4.2 Measurement of Air Velocity

The airflow rate was measured using a hot wire anemometer (Kurz Instruments, USA) with a sensitivity of ± 0.25 m/s placed at the inlet section of the drying chamber. The air velocity profile across the drying chamber was evaluated for the uniformity of airflow.

2.2.5 Drying Procedures

Drying experiments were performed under different conditions of the drying air. The effect of process parameters such as temperature, humidity, and velocity of the drying
air was studied. The temperatures tested were 60-90°C. Three sets of humidity (3, 28 & 46%) and four levels of airflow ranging from 1 to 4 m/s were investigated. These conditions were selected to cover the range of typical drying conditions employed commercially as discussed in chapter 7. Prior to each drying run, the samples were washed with water and allowed to equilibrate under room conditions overnight. The fruit were uniformly spread on the tray in a single layer and loaded into the drying chamber after the desired drying conditions had stabilised. The sample size for each run was approximately 800-1000 grams (50 fresh plums). Each drying run was carried out past the normal moisture content of commercial dried prunes (i.e. 18-20%, dry basis) in order to study the entire drying process. All the experiments were carried out at least twice to ensure reliability and the mean was used for data interpretation.

2.2.6 Moisture Content Determination

The initial moisture content of the plums was determined using a standard method by vacuum drying at 70°C for 6 hours over a magnesium sulphate desiccant. This was repeated seven times to obtain a mean result. The initial moisture content (MC_{w.b}) was expressed on a percent wet basis.

2.3 RESULTS AND DISCUSSION

2.3.1 Preliminary Drying Experiments

Preliminary drying experiments were conducted using a conventional laboratory air oven to initially assess the drying characteristics of plums under different conditions of drying air. Figure 2.3 shows the results of the effect of temperature upon the kinetics of drying plums. Clearly, the mass loss versus time curves indicate the large effect of utilising elevated temperature. It can be seen that the initial rate of drying at 100°C is over twice that at 80°C. The average initial moisture content of the plums used for this study was found to be about 67.9 (±1.1) % on wet weight basis including the seed. For prunes commercially dried down to about 20% final moisture content (in dry basis), this corresponds to 61.5% mass loss. This would lead to a substantial difference in apparent drying time from 12 hours at 80°C to just around 6 hours at 100°C.
Figure 2.3. Effect of drying air temperature on the kinetics of drying plums using conventional air oven (Rh<5%; V<0.3 m/s).

Comparison of the drying kinetics at 80°C under different humidity conditions is shown in Figure 2.4. This study was initially conducted to ascertain the effect of moisture content in the drying air upon the rate of drying. It was observed from the results that the relative humidity condition has a profound effect upon the initial rate of water removal. Although there was poor control of the humidity conditions it showed however that the initial drying rate decreases with increase in relative humidity of the drying air. In terms of expected drying time to reach a final moisture content of about 20% in dry basis (equivalent to 61.5% mass loss), the drying at low humidity condition took about 8 hours whilst at medium humidity it took 12 hours. This would result to a difference of around 4 hours. Clearly, the result shows the advantage of utilising lower humidity during the air drying process.

The recorded mass loss data for two replicates indicated some scattering. In all cases, the standard deviation for two replications was in the range of 1-7%. Under this system of drying, it was not possible to accurately control and maintain the relative humidity of the drying air such that it was a constant. Figure 2.5 shows typical changes in humidity.
Figure 2.4. Effect of relative humidity of the drying air on the kinetics of drying plums using conventional air oven (T=80°C; V<0.3 m/s).

Figure 2.5. Relative humidity changes of the drying air at 80°C using the conventional air oven (V<0.3 m/s).
during drying at 80°C under the three different humidity conditions. It can be seen that there was always an initial increase in relative humidity as water evaporated from the high-moisture plums. Opening of the oven door during sampling may had also contributed some variations in the drying conditions. In addition, it was not also possible to study the effect of air velocity, as there was no means of controlling the speed of the fan. These clearly show a need of a more sophisticated experimental drying system to be able to study precisely the effect of different drying conditions and to obtain more accurate data.

2.3.2 Performance of the Improved Experimental Dehydration System

Shortcomings of a conventional simple laboratory drying system led to the development of an improved drying system. In most drying studies it is desirable to maintain constant drying conditions throughout each drying run in order to obtain representative drying kinetics of the material for a particular drying condition. In this work, a computer-based experimental drying system was specifically developed and tested to study the kinetics of drying plums under carefully controlled drying conditions. The setup was designed to allow typical commercial prune dehydration to be simulated. It can be operated over a wide range of drying conditions. The concept of convective air-drying was adopted in which hot air is forcefully blown into the product to remove the moisture.

Prior to the drying experiments, the performance of the experimental drying system was evaluated particularly the temperature/humidity sensing component. Although the commercially obtained temperature/humidity probes had been fully calibrated at the factory, it was necessary to check its accuracy regularly to ensure that it met the manufacturer's specification. Preliminary trial runs of the drying system were made after its components were completely tested and installed to ensure smooth operation during the actual drying experiments. After several minor adjustments, the setup was continuously used for several months in a year and found to work well throughout the experimental period. The use of a computer-based data acquisition system gave valuable drying information in extremely accurate time intervals. Four signals were regularly monitored by the data acquisition system. These were the mass of the sample being
dried in the chamber, the temperature and humidity of the drying air at the inlet and outlet sections of the drying chamber and the ambient conditions.

The new drying system had a maximum attainable drying air temperature and relative humidity of 100°C and 46%, respectively. It could be operated with an air velocity of up to 5 m/s. These conditions were enough to cover the drying conditions employed in a typical prune dehydration tunnel. Typical drying data obtained using the experimental setup are depicted in Figure 2.6.

![Graph showing drying data](image)

**Figure 2.6.** Typical drying data obtained using a computer-based experimental dehydration system (V=1 m/s; MC_{w,b}=69%).

As can be seen from the figure, the drying conditions were maintained at a relatively constant level throughout the drying period. The drying conditions were monitored at the inlet section of the drying chamber prior to the sampling tray. From the analysis of the recorded data, the drying air temperature showed small fluctuations but was always contained within ± 0.5°C. The relative humidity of the drying air oscillated at most ± 3% particularly at the highest humidity level. This is because of the on/off sequence of the heating system, which causes fluctuations in the evaporation of water injected into
the heating system. At lower humidity levels where there was less or no application of water into the heating system the observed fluctuations were generally much lower (about 0.5%). The regulation of the air velocity was within ± 0.25 m/s. Moreover, the figure illustrates the representative drying curves of plums for two runs corresponding to these conditions. Both of the observed mass loss curves showed continuous and smooth patterns. There was no significant deviation between test replicates. In all drying cases, the standard deviation of mass loss for two replications was in the range of 0.1-1.8%. Given the natural variation of plums this represents very good reproducibility.

2.3.3 Effect of Process Parameters on Drying Kinetics

2.3.3.1 Drying Air Temperature

Laboratory-scale drying experiments were conducted to investigate the kinetics of drying plums under different drying air temperatures. During the experiments the relative humidity of the drying air was kept at least below 3% whilst the air velocity was maintained at about 1 m/s. Figure 2.7 depicts the mass loss profile of plums dried at various drying air temperatures.

The results clearly indicate the large effect of drying air temperature upon the drying kinetics as has been commonly found in most biological products. Obviously, the rate of drying increases with increasing temperature resulting in reduction of the total drying time. The total drying time is the time required to dry the material down to a desired moisture content level safe enough for storage. Prunes are often dried to about 20% (dry basis) moisture content commercially. In this study, the average initial moisture content of the plums was found to be 69% wet basis (±1.5%). For prunes with this initial moisture content, a mass loss of 62.8% corresponded to moisture content of 20%. Analysis of the curves shows that the plums dried to 20% moisture content at 60°C took about 2845 minutes, 1190 minutes at 70°C, 890 minutes at 80°C and just under 550 minutes at 90°C. The result indicates that the initial rate of drying plums at 90°C is two times that at 70°C. This would lead to a reduction in apparent drying time of around 10 hours. Increasing the temperature from 70°C to 80°C would shorten the total drying time by about 5 hours.
The influence of temperature on the drying kinetics of plums has recently been reported.\textsuperscript{22, 75} The Barbanti experiments have shown the effect of composite drying on the specific drying kinetics of plums. They have found no significant difference in utilising two regimes of drying temperature. The work of Newman et al\textsuperscript{75} has initially demonstrated the effect of temperature on the drying kinetics of plums. However, in their experiments the velocity of the drying air was very low (about 0.3 m/s) and the humidity of the drying air was not closely monitored or controlled. Despite these facts, their results indicated similar trend to the data obtained from this study of using an improved drying system. For instance, Newman and co-workers\textsuperscript{75} found a 60\% mass loss at 90°C after 7 hours of drying. Results from this study recorded a 58\% mass loss after the same period at 90°C. The slight discrepancies could be attributed to the difference in other drying conditions (particularly air velocity) apart from the variation between plum samples. However, the present results would eventually give much clearer picture of the drying kinetics of plums as drying conditions were closely controlled and that the drying kinetics were monitored in shorter intervals and over a much longer period. This would enhance further understanding of the entire drying process of plums.
The result in Figure 2.7 is notable in that there appears to be an enormous advantage in utilising a higher temperature in terms of the production throughput because of the considerable reduction in drying time. However, it should be borne in mind that employing elevated drying temperatures could possibly result in an inferior quality of final product. The consequences of using higher temperatures were initially verified by assessing the physical characteristics of the plums after each drying run. Generally, plums were found to shrink continuously during the drying process. This is obvious, as large quantity of moisture, which occupies a considerable volume, has to be removed from the fruit. Shrinkage starts to become visible after the fruit has lost 20-30% of its moisture. The appearance of plums dried at 80°C temperature and below was very shriveled and dark in color as well as being hard. Most of the plums dried at 90°C appeared to have reinflated to their original shape. They were light in density and inside had a texture of charcoal. This observation seems to indicate that at elevated temperature there appears severe alteration of the chemical composition of the fruit. This phenomenon is corroborated by the fact that for the extended drying time at elevated temperature the mass loss even exceeded beyond the initial moisture content. It was found that the experimental mass loss at 90°C reached 71% (2% above the initial moisture content). Heat damage was more prominent at 90°C temperature as severe skin splitting, bleeding and loss of juice were further noted. About 30% of the plums were observed to burst at the early stages of drying at this temperature.

Another distinctive feature between drying curves was the large difference in drying observed between 60°C and the higher temperatures. From the result, it appears that lowering the temperature from 70°C to just 60°C would stretch the drying time to over 27 hours. This is a substantial difference, which could be attributed to the efficiency of cell disruption particularly in the waxy skin layer of the fruit induced by drying. Many of the waxy fruits (i.e., grapes, plums, berries, etc.) have been shown to possess a skin layer structure different from those underlying tissues which is hydrophobic in nature. The hydrophobicity of the skin layer provides a significant barrier to water movement during drying. It may be suggested from these results that a drying air temperature of 60°C was inefficient in rupturing the waxy skin cell structure so that its water-barrier properties may be still at play. This limits the maximum drying potential under this condition.
Generally, the results of this experiment reveal that for thermolabile foodstuffs, particularly fruits, there is a maximum permissible temperature, beyond which the product may undergo undesirable changes. Consequently, these changes would result in inferior quality product upon rehydration. The results also suggest that at 70°C and above there is much easier movement of water through the skin.

### 2.3.3.2 Drying Air Velocity

The effect of air velocity was then examined at constant temperature (70°C) whilst the relative humidity of the drying air was maintained below 3%. Time dependent mass losses of plums during drying at different air velocities are plotted in Figure 2.8.

![Figure 2.8. Effect of air velocity on the kinetics of drying plums (T=70°C; Rh=3%; MC\_iw=69\%).](image)

The figure clearly illustrates the effect of air velocity upon the drying kinetics of plums. It is evident from the figure that the air velocity had a significant effect on the initial rate of drying. However, in terms of the total time drying time to reach a 20% final moisture content (about 62.8% mass loss), the influence of drying air velocity appeared to be
relevant only between 1 m/s and 2 m/s. A pronounced difference of about 2 hours was recorded between 1 m/s and 2 m/s. As the airflow rate increased, the variation in drying behaviour became less distinct, and there was very little difference above 62.8% mass loss particularly between 3 m/s and 4 m/s. For example, drying to 62.8% mass loss with an air velocity of 3 m/s would take 1040 minutes whereas at 4 m/s the drying time would be about 1025 minutes. A difference of around 15 minutes is small compared to the overall drying time.

It would therefore appear from the results that the effect of air velocity to enhance the drying process seems limited to a certain level. Hence, any further increase in air velocity above this level would not result in any worthwhile improvements. The most recent published work looking at the effect of air velocity on the drying kinetics of plums was reported by Barbanti and co-workers. Some of their experiments were conducted on Ente, a type of plum similar in size to d’Agen. However, it was difficult to draw direct comparison with their results due to the fact that they were using two temperature regimes and do not quote the air humidity conditions. Their work studied two levels of velocity (1.5 m/s & 4.5 m/s). It indicates though an increased drying rate in the early stages of drying with an increase in air velocity as found in the present work.

The effect of air velocity on drying behaviour of other foodstuffs has been well substantiated by numerous researchers. McMinn and Magee observed a limited influence of air velocity on the rate of drying potato. They found that during drying of potato at 60°C down to a moisture content of about 75% (dry basis), it took about 600 minutes at 0.5 m/s whilst 570 and 450 minutes at 1 and 1.5 m/s, respectively. In addition, Mullet et al established the presence of critical velocity values above which the presence of external resistance was negligible. In the dehydration of carrots, these authors obtained a critical gas flow rate of approximately 6000 kg/m² h after which further increase in gas flow rate had negligible effect. Rosello et al found a critical gas flow rate of 8000 kg/m²h in drying of potato at 50°C.

The result of this experiment connotes that the role of the external resistance to moisture transport becomes negligible compared to the internal resistance as the air velocity increases. It should be noted that the air stream only facilitates drying by removing
moisture reaching the surface. Thus, the effect of air velocity seems to be limited to a certain level and any further increase in velocity above this value would not result in considerable reduction in drying time. For instance, during the initial stage of drying, there is abundant free water within the fruit, and a large amount of air is the main requirement. As the fruit dries, internal resistance to the mass transfer becomes the governing mechanism and higher temperatures rather than airflow, are more efficient in squeezing the remaining moisture.

The observed diminishing influence of air velocity on drying rate could also be explained by the well-known case hardening which tends to seal the skin preventing diffusion of moisture through the surface. Barbanti et al. 22 studied the effect of velocity on drying of plums and found that at the later stages of drying the rate of moisture loss for higher velocity became slower than that at lower velocity, which could be attributed to case hardening. High airflow rate possibly triggers scorching and drying out of skin making it less permeable to moisture transport. According to McBean et al. 98 if the water is removed from the surface too rapidly from the drying surface, capillaries may be closed so quickly so that water movement from the interior is hindered.

2.3.3.3 Drying Air Relative Humidity

The effect of relative humidity of the drying on the drying kinetics of plums was then investigated. In all cases the drying air temperature was kept constant at about 70°C and velocity was maintained at 1 m/s. Figure 2.9 illustrates the apparent dependence of the drying rate upon the relative humidity of the drying air. It further shows that under higher humidity conditions the rate of drying was lower. In terms of total drying time required to reach a final moisture content of 20% (about 62.8% mass loss), the drying of plums at 46% humidity took 1400 minutes, 1315 minutes at 28% humidity, whilst at 3% humidity, the total drying time was 1190 minutes. This represents a difference of about 3.5 hours between the extreme humidity conditions, which is significant.

Studies on the effect of relative humidity on the drying kinetics of some foodstuffs have been reported. Morita et al. 99 investigated the effect of air relative humidity in the range of 20 to 75% on the rate of drying rough rice. They found a significant decrease in
drying rate with increasing relative humidity. For instance, during drying at 40°C the initial drying rate at relative humidity of 30% was about 75 (kg H₂O/kg dry matter/h) whilst at 75% it was just around 40 (kg H₂O/kg dry matter/h). Lamberg also studied the effect of relative humidity in the range of 1 to 49% on the rate of drying potato at temperatures of 60-99°C and found significant decrease in drying rate with increasing relative humidity.

![Figure 2.9](Image)

**Figure 2.9.** Effect of air relative humidity on the kinetics of moisture loss during drying of plums (T=70°C; V=1m/s; MC_{iwb}=69%).

In a thermodynamic sense, decreasing the moisture content of the drying air increases the potential of the drying air to pickup and remove moisture from the product. This is because the reduction in the humidity of the drying air increases the initial moisture concentration gradient between the fruit and the drying air. Consequently, this leads to an increase of the driving force for mass transfer from the fruit surface to the air stream. It is therefore possible to substantially reduce the overall drying time hence increasing the product throughput by merely decreasing the moisture content of the drying air. The striking difference in drying kinetics between humidity levels also demonstrates the
importance of monitoring and possibly controlling the drying air humidity during commercial drying of fruit.

2.3.3.4 General Discussion

It has been shown in the previous section that the drying process parameters (i.e., temperature, velocity and humidity) greatly influence the kinetics of moisture loss of plums during drying. The kinetics of the drying process can be better illustrated by plotting the drying rate versus moisture content. This approach allows one to clearly characterise the behaviour of drying. In previous studies, drying rates have been estimated by numerical differentiation of the mass loss curves using three-point formulas.101-103 This was performed by fitting a quadratic function to three consecutive points and then differentiating the result. In this current study the drying rate curves were obtained by fitting portions of the mass loss data to a linear function. The number of consecutive points used in this fitting was varied from 3 to 11. It was found that seven points gave the optimum results in terms of lowest residuals for least-squares analysis and in excellent agreement with the quadratic fit method.

Figure 2.10 shows a typical example of the drying rate versus moisture content plots derived from mass loss data. It is indicative from the figure that the rate of moisture removal exhibits distinct features. The drying rate followed a pattern in which there was an initial rapid increase in drying rates at the beginning of the drying process as equilibration is taking place. This was proceeded with a near gradual levelling off thereafter depending on the operating conditions followed by a declining pattern. At elevated temperature the abrupt rise in drying rate was proceeded immediately by a declining rate pattern. So-called constant rate behaviour was not apparent at higher temperature presumably due to the fact that drying was so vigorous that a water depletion layer formed very quickly. The existence of a constant period was more visible at milder drying temperatures. In all cases, rapid removal of moisture took place during the early stages of drying as a consequence of greater concentration gradients between the drying air and the fruit. This is because of the initial higher concentration of moisture within the fruit matrix. The subsequent extraction of the remaining moisture in the latter stages of drying was very sluggish since the last traces of moisture had to be
removed under low concentration gradients as the moisture concentration within the fruit approaches near equilibration with the environment.

**Figure 2.10.** Effect of air temperature on the rate of drying ($V=1\text{m/s}; \text{Rh}=3\%$; $\text{MC}_{\text{wb}}=69\%$).

In theory a period with a constant rate of drying signifies a process mainly controlled by the external resistance to moisture transfer. This means that the properties of the drying air predominantly limit the rate of drying. In this case, the rate of water evaporation from the surface to the drying air can be treated similar to that of the evaporation of free water. However, in some cases there may be possibly a constant supply of moistures from the interior to the fruit surface which are readily available for surface evaporation but the rate may be much lower compared to the maximum evaporation potential of free water. According to Achanta and Okos the vapour pressure exerted by the material is always lower than that exhibited by free water hence a strict constant-rate period is necessarily precluded. This phenomenon was considered further by determining the evaporation rate of free water under the same drying conditions.
Results reveal that the evaporation potential of the free water is greater than the observed maximum drying rates of plums under the same drying conditions (Figure 2.11). This indicates that the moisture loss process at the early stages of drying may be affected by other factors particularly at lower temperatures. The fact that there was a relatively large quantity of moisture initially within the fruit, it was speculated that the skin of the plum may have provided significant barrier to moisture transfer. This was verified by examining the rate of drying between plums with and without skin.

![Graph showing evaporation rate](image)

**Figure 2.11.** Maximum evaporation rate from free water and plums at different drying air temperatures (Rh=3%; V=1m/s).

It is interesting to note that the plums without skin dried much faster than those plums with intact skins (Figure 2.12). Results indicate that the initial drying rate of peeled plums was twice over than the unpeeled plums. This vindicates that the rate of water transport across the waxy skin layer lagged behind the movement of water within the flesh, which means that the skin is somehow governing the drying mechanism. This phenomenon is more prominent at the early stages of drying. Obviously, the ability of the skin to suppress moisture diffusion depends partly on the degree of its cell disruption at the surface induced by thermal heating.
McBean et al.\textsuperscript{39} showed that the prune wax coating on the skin (structure responsible to the restrictive effect to water movement across the skin layer), as a whole does not melt or become disrupted until about 65°C. In the present study, it was found that the surface temperature of the plum during drying increased quite rapidly in the first 30 minutes to about 5-8°C below the set drying air temperature and leveled off thereafter (depending upon the temperature) then gradually increased with time in the later stages of drying (Figure 2.13). At 80°C and above the fruit surface temperature quickly reached above 65°C, whilst at 70°C, the surface temperature of the fruit levelled off at about 63°C for 10-11 hours before increasing to reach near the set drying temperature. At 60°C, the fruit surface temperature rapidly increased to about 55°C and maintained this level throughout the 18-hour drying period. It is worthwhile noticing that the period at which the fruit temperature exhibited constant behaviour is consistent with the constant-rate period of drying. If the skin layer is affecting the drying process during the constant period then the rate of moisture loss is likely influenced by the degree of cell disruption of the skin layer. This means that the restricted effect of the skin to water passages is a
function of the drying air temperature. Thus increasing the drying air temperature would tend to diminish the significance of the skin layer to hinder the moisture transfer process.

![Figure 2.13](image)

**Figure 2.13.** Surface temperature profile of plums during drying at various air temperatures (Rh=3%; V=1m/s).

The likely dependence of the skin permeability to water on the degree of heating is also exemplified at different conditions of drying air (velocity and humidity). In all cases it was observed that the differences in drying rates were more dramatic at the early stages of drying. It should be noted that the early periods of drying were closely linked to the operating conditions (i.e., temperature, velocity and humidity). During the final stages of drying an internal mass transfer mechanism prevails. In general, the remarkable variations in the drying kinetics between different drying conditions suggest a great potential for improvements of the commercial process. Because of the seemingly obvious role of the skin layer on the drying process, it is interesting to investigate the water permeability across the skin layer at different stages of drying.
The skin layer of plums appears to have a marked influence on the rate of moisture loss during drying. In this study, the integrity of the plum skin to act as a water barrier during drying was further verified experimentally. The water permeability across the skin of plums was studied employing a radiotracer technique. The skin of fresh and partially dried plums was tested. Fresh plums were dried using the experimental setup described in the previous section. A plum sample was cut into halves along the longitudinal axis in order to obtain maximum surface area. The pulp was then manually scraped and removed from the waxy skin layer. The thickness of the skin layer was determined using a hand-held micrometer. The average thickness of the plum skin was found to be 0.53 mm (± 0.01).

A diffusion cell shown in Figure 2.14 was used for the experiment. It consisted of two compartments separated by a membrane (in this case a plum skin). One side of the cell
was used as the compartment for the source solution where the tracer was introduced. The other side acted as the compartment where the concentration of the diffusing tracer was constantly monitored. The effective membrane surface area was about 3.14 cm². The compartments were made of cylindrical glass mounted into a Teflon block. They were clamped together using four screws. The skin sample held between the two blocks was positioned in such a way that its waxy surface was facing towards the receiver side of the cell to emulate the actual movement of moisture in plums during drying. The tightness between the two compartments was achieved without damaging the skin sample via a rubber O-ring. The diffusion cell was then mounted on a magnetic stirrer unit and a magnetic stirring bar was placed on each side of the cell to provide thorough mixing. An open wire mesh was placed just before the skin sample on both sides to prevent damage due to the rotating action of the stirring bar.

Prior to each experiment, both sides of the cell were filled with milli-Q water (10 MΩ cm⁻¹) of about the same volume (15 mL) and allowed to equilibrate overnight. Radio-labeled water (³H₂O) tracer (20 µL) was then added into the source side of the cell. The radioactivity in the receiver solution was continuously monitored by taking 50 µL of sample at predetermined time intervals. Thorough cleaning of the syringe with Milli-Q water after each sampling was done to avoid contamination. Each sample was transferred into the vial containing 16mL of scintillant. The amounts of tracer and the BCS scintillant used were predetermined experimentally to obtain reasonable radioactivity detection. BCS scintillant and ³H₂O were obtained from Amersham Australia Ltd.

The concentrations of tracer in the sample (in 20-mL glass vial) were measured using a standard liquid scintillation counter (LKB-Wallac 1219 Rackbeta). Reproducibility of the experiments was determined by making up 8 replicate solutions of the same volume containing the same amount of tracer. A 5mL sample was taken from a 250mL solution containing 10 µL of tracer (³H₂O) and was added to 200mL scintillant. Eight samples of 16 mL each were drawn from this solution and were analysed. Each replicate was weighed to check any volume discrepancies. The reproducibility was found to be about ± 1%.
A calibration was carried out by preparing four solutions of different tracer concentrations. A 1mL sample taken from 100mL aqueous solution containing 10 μL of tracer was added to 100mL, 250mL, 500mL & 1000 mL of milli-Q water. Fifty μL of sample from each solution was taken and filled into the sampling vials containing 16mL of BCS scintillant and were analyzed.

![Count vs Time Graph](image)

**Figure 2.15.** Effect of drying on water permeability of plum skin using radiotracer method (T=70°C; Rh=3%; V=5m/s).

The result of the experiment is portrayed in Figure 2.15. Each data set was the average of at least two replicates. Results indicate that the skin of the fresh plum is permeable to water. Drying of plums at 70°C for up to 2 hours resulted in insignificant alteration in the skin permeability relative to the fresh plum sample. On drying further for 3-5 hours, there was substantial increase in the skin permeability. However, it was not possible to continue the experiments beyond 5 hours because of the difficulty associated in extracting an intact skin sample. These results though illustrate the level of disruption inflicted on the (waxy) skin layer by thermal heating. Raising the temperature increases the permeability of the skin perhaps through cell rupture. Under the conditions used in the experiment, the plum surface temperature rose rapidly and leveled off to about 62°C.
for about 2 hours then gradually increases thereafter as it approaches near the set drying air temperature value (Figure 2.16). This is in agreement with the work of McBean et al.\textsuperscript{41} who observed significant disruption of the waxy portion of the skin layer at this temperature. The fruit temperature profile closely matched with the skin permeability trend and further confirms the dependence of the efficiency of cell disruption on the degree of heating. The result implies that the waxy skin layer of the plums may play a crucial role in the drying process particularly at the early stages of drying where there is probably easy movement of abundant moisture within the flesh.

![Figure 2.16. Surface temperature profile of plum dried at 70°C (Rh=3%; V=5m/s).](image)

This is consistent with suggestions that for fruits having waxy coatings on the skin surface (i.e. apples, grapes, plums, etc.) the skin layer is resistant to passage of water or water vapor and represents a significant barrier to moisture transport. This has been shown in the studies of several authors.\textsuperscript{7, 41, 46} The magnitude to which the rate-controlling properties of the skin affect the drying process seems to depend upon the drying conditions. When all the free water is depleted the diffusion rate-controlling mechanism within the flesh starts to dominate. At this point the effect of skin layer becomes insignificant. Accordingly, Aguilera\textsuperscript{48} pointed out that as the moisture content
decreases the waxy cuticle plays a smaller role as a rate-controlling factor of the drying process. It is therefore interesting to consider further the characteristics of water transport within the flesh.

Figure 2.17 illustrates the diffusion coefficient of water in the flesh of the plum as a function of moisture content at 25°C measured using NMR spin-echo techniques. This is the data of Back and Price\textsuperscript{105} who kindly agreed for it to be used (and reproduced here) prior to publication. Each data point shown in this figure is an average of at least three determinations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diffusion_coefficient_graph.png}
\caption{Diffusion coefficient of water in plums obtained from NMR spin-echo technique (Back and Price\textsuperscript{105}).}
\end{figure}

The results indicate high moisture mobility within the flesh in fresh plums (equivalent to a moisture content of about 2.23 kg H$_2$O/kg dry matter) compared to the dried plums (0.61 kg H$_2$O/kg dry matter). It shows that as plums dried the ease of movement of water within the flesh decreases. For fresh plums the diffusion coefficient was found to be about 1x10$^{-9}$ m$^2$/s. Plums dried to a moisture content of around 50\% (dry basis) were observed to have a diffusion coefficient of 2x10$^{-10}$ m$^2$/s. The self-diffusion coefficient
of water at 25°C was reported\textsuperscript{106} to be $2.234 \times 10^{-9}$ m$^2$/s. This means that the diffusivity of water within the flesh in fresh plums is twice as slow as the self-diffusion of water at the same temperature. It also shows that water mobility within the flesh of plums dried to 50% moisture content is about 5 times slower compared to that of fresh plums. The slower diffusion of water in the later part of drying may be partly explained by a more tortuous path encountered and probably due to the restriction imposed by the compression of cells as a result of shrinkage. This is consistent with the observed initial rapid moisture loss during drying and the subsequent decreasing rate in the later stages.

In an attempt to elucidate the rate-controlling mechanism of moisture loss during drying, the mobility of water between the flesh and across the skin was compared. Permeability of water across the skin layer was estimated using the data in Figure 2.15 and was expressed in terms of diffusion coefficient. The diffusion coefficient was determined by applying the diffusion equation for a plane sheet in which $J=(D/L)(C_1-C_2)$ where $J$ is flux, $D$ is diffusion coefficient, $L$ thickness of the skin, and $C_1$ and $C_2$ are concentrations in each side.\textsuperscript{107} Results of the approximation are shown in Figure 2.18. Comparison between this figure and Figure 2.17 indicates significant differences in diffusivity of water between the skin layer and the flesh. It can be seen that the water diffusivity within the flesh is generally higher than at the skin layer. For fresh plums, it was found that the diffusion coefficient within the flesh was around 35 times higher compared to that at skin layer.

The results may be partly explained by the length of the diffusion path in which the water is diffusing. In NMR measurements, molecular diffusion may take place in a short time interval between the two gradient pulses. Depending on the length of time of observation, the average path distance in which a molecule travels during this period may be comparable to the size of the cells. Hence the moisture diffusion coefficient obtained from NMR measurements might correspond only to the movement of water molecule just within the cell. It should be noted that the water molecule might diffuse not only within the cell but also through the cell wall, membranes, etc in which the diffusivity may be different.\textsuperscript{108} Usually, the boundaries of the cells would impose greater barrier to water movement than within the cell.
It is also interesting to observe that as the drying progresses, the movement of water within the flesh is increasingly restricted whilst at the skin layer the restriction of water transport is decreasing. This results in a decreasing difference in water movement between the skin and the flesh in the later stages of drying. For example, for plums dried to a moisture content of about 0.60 kg H$_2$O/kg dry matter it was found that the skin diffusion coefficient was about 9.7x10$^{-10}$ m$^2$/s compared to around 2x10$^{-10}$ m$^2$/s for the flesh. Thus at the last stages of drying the mobility of water within the flesh becomes the important factor. The above results further confirm the significant role of the skin layer in the moisture loss process particularly at the early stages of drying and suggest the existence of mobile water molecules within the flesh.

The principles and applications of NMR technique in food systems have been reviewed in a number of articles.\textsuperscript{109-112} It has been applied to follow the transport of water during air drying of foods.\textsuperscript{110, 113, 114} For instance, Fukuoka et al\textsuperscript{108} estimated water diffusion in a dry soybean seed which has a moisture content of about 14\% (dry basis). They observed a constant diffusion coefficient of 4.3x10$^{-10}$ m$^2$/s. Using NMR imaging, the
Deff values for a potato during drying were found to be $1.04 - 7.28 \times 10^{-10}$ m$^2$/s for moisture contents between 40-55% (wet basis) at $40^\circ$C.\textsuperscript{115} Callaghan et al\textsuperscript{116} measured water diffusion in wheat grains using PFG-NMR with a short diffusion time (>10 ms) and found the diffusion coefficient to vary from $1.8 \times 10^{-10}$ m$^2$/s at 25% moisture content (dry basis) to $1.2 \times 10^{-9}$ m$^2$/s at 50% moisture content. PFG-NMR was also used by Stapley et al\textsuperscript{117} to characterise the diffusion of water within the samples of carrots conventionally heated.

The significant variation on the rate of moisture loss could also be further explained by the changes in cellular structure of plums occurring during drying. According to Martin and Junifer\textsuperscript{118}, the complex shape of the overlapping wax platelets in the skin layer and the resulting confrontation of that region forces the evaporating water to take a tortuous path. Bain and McBean\textsuperscript{8} followed the structural changes of the surface wax during drying of d'Agen plums using carbon replica and thin-sectioning techniques of electron microscopy. They followed the structural changes of the surface wax as the temperature was increased from 49 to $77^\circ$C and found some structural degradation at $54^\circ$C but was not completely disrupted until $66^\circ$C. The unpublished findings of Storey and Price\textsuperscript{119} showed some distinct alterations of the skin layer structure of plums as drying progresses using SEM. They also followed the micro-structural changes of the underlying pulp tissue and observed significant collapse of pulp cells, degradation of membranes and pronounced swelling of the cell wall. In a high moisture cellular material such as plant tissue, moisture must migrate from the protoplasm through the cell membrane and surrounding wall and across the porous structure of the tissue.\textsuperscript{48} Intact cell walls and adhering membranes usually constitute a major resistance to water diffusion. Hence the degradation of cell membranes might also facilitate easy movement of water within the flesh.

The alterations in the micro-structural level that were observed by these authors might explain at least partially the moisture loss process during drying. It shows that the early stages of drying may be enhanced by weakening the integrity of the cell walls to restrict water movement in conjunction with the fracturing of the skin layer. Higher drying rate at this stage of drying may be also influenced by the structural changes of the wax
coating induced by drying. These changes might transform the water-resistant properties of the wax coating. During the last stages of drying, the water movement may be greatly impaired by the compactness of the microstructure. The collapse of cells tends to seal the diffusion pathways. This could partly explain the enormous difficulty of moisture to diffuse to the surface particularly during these stages of drying. These are consistent with the experimentally observed rapid loss of moisture at the early stages of drying and the subsequent slow rate at the last stages of drying.

2.3.5 Water Loss Profile during Ambient Storage

This experiment was conducted to investigate the rate of water loss under ambient storage conditions for partially dried plums in an effort to establish further any relation between the skin permeability and water movement within the flesh. Plums were dried at different temperatures and times using the experimental setup previously described. Three drying temperatures were studied: 60°C, 70°C and 80°C. Drying experiments were terminated at various times: 2, 4, and 6 hours. After drying, samples were allowed to cool at room temperature before weighing. These were then stored at ambient conditions uniformly spread on trays in a single layer. The change in mass was continuously monitored at 1-day interval over a period of 20 days. Weighing was carried out using an electronic balance (Denver Instruments, USA) which had a sensitivity of ± 0.0001 g. Five plums were used for each experiment and were averaged.

The result of the experiment is presented in Figure 2.19. Again, the effect of drying on the skin permeability is obvious. As seen from this figure, the rate of mass loss under the same storage conditions for plums partially dried at 70°C was relatively higher than those dried at 60°C. This phenomenon may be ascribed to the level of thermal damage to the waxy surface given the fact they were dried to the same moisture content level. The plot further shows that for the plums dried at elevated temperatures for longer times the effect of skin disruption due to heating is not visible. Though there may be considerable disruption of the skin structure of the plums dried under these conditions, because of the lower moisture concentration within the fruit, the driving force for mass transfer becomes less as the moisture concentration of the fruit approaches equilibration with the ambient conditions. This suggests the reliance of the mass loss process on the
internal diffusion rate-controlled mechanism as manifested by the slowing rate indicated from the divergence of these curves.

**Figure 2.19.** The rate of mass loss during ambient storage of plums partially dried at different temperatures and times (Rh=3%; V=5m/s; MC\text{wib}=66%).

### 2.3.6 Influence of Initial Moisture Content on the Drying Kinetics of Plums

The kinetics of drying plums of differing initial moisture content were studied. It was carried out because the moisture content of plums during harvest may vary between seasons depending on the climatic conditions. The drying experiments were carried out during two harvest seasons. Fruit harvested during the 1996 season were found to have an average initial moisture content (wet basis) of 69 (±1.5)% while the 1997 season produced plums with an initial moisture content of 66 (±1.5)%. Typical drying curves for plums with different initial moisture content are illustrated in Figure 2.20. The drying rates were initially higher for plums with higher initial moisture content. This is because the total available water for drying is initially greater. As a consequence, the initial concentration gradient is higher resulting to greater driving force for water transport.
Figure 2.20. Effect of initial moisture content on drying kinetics of plums (T=70°C; Rh=3%; V=1m/s).

Probably, the increase in initial drying rate at higher initial moisture content compensates the difference. Thus, this variation did not result in elongation of the drying process. The results indicate that the overall drying time for both initial moisture contents required to reach a final moisture content of 20% (dry basis) was almost identical: 1190 minutes (69%) compared with 1170 minutes (66%). This is in accordance with the results obtained by Barbanti et al.\textsuperscript{23} who concluded that the specific drying kinetics of different plum cultivars were not influenced by the initial moisture content.

2.4 CONCLUSIONS

A comprehensive study on the kinetics of drying plums was attempted in order to obtain better understanding of the mechanism controlling the process. The study has shown that the process parameters greatly influenced the drying kinetics of plums. The drying rates were very much affected by the drying air temperature. Drying above 70°C is ideal but the use of elevated temperatures (90°C and above) could be detrimental. Increasing
the air velocity above 2 m/s did not markedly enhance the drying process. At lower drying air humidity, the drying process was notably reduced. The distinctive variations in the kinetics of moisture loss during drying over the range of drying conditions studied demonstrate the importance of determining the optimum operating conditions. This clearly manifests the need to closely monitor and better control the conditions during commercial drying of fruit.

The mass transfer during drying of plums is characterised by the removal of moisture from the fruit surface, transport of moisture across the waxy skin layer and diffusion of moisture within the fruit matrix. The mechanism of drying is affected by the nature of the waxy skin layer particularly at the early stages of drying. Thermal heating increases the skin permeability. The extent to which the rate-controlling properties of the waxy skin are significant depends on the drying temperature owing to the efficiency of cell disruption. At the later stages of drying internal mass transfer appears to be the governing factor. This mechanism is more influenced by temperature, while the velocity and humidity of the drying air are of minor significance.
MODELLING THE DRYING PROCESS OF PLUMS
3.1 INTRODUCTION

The factors affecting the kinetics of drying plums have been extensively studied in chapter 2. In order to gain more insight and better understanding into the mechanism involved in the drying process of plums it is necessary to develop a physical model to represent its behaviour. Modelling is a means of describing the phenomenal aspects involved in the process to interpret the observed data and to predict the behaviour under different conditions. It is of much use to the drying industry and a very useful way to validate mechanisms of drying. A reliable model often can prevent or minimise costly mistakes in prototype development. Models can also be used in the control of a process. During drying other chemical reactions, which for most foodstuffs are likely to be dependent on moisture content may be important. For foodstuffs like fruits most of these reactions could result in inferior quality of the final product. Undesirable effects may be avoided or at least minimised and the process could be better controlled if moisture content in foods with respect to time could be accurately predicted. From a commercial point of view it is probably more useful to predict the time required to dry a particular foodstuff for a given drying condition.

With the proliferation of computers and the increasing need for efficient process, the use of mathematical models in industrial processes is widespread. Much effort has been made in the last 20-30 years to model the drying processes of foodstuffs. Usually, mass transfer alone has been found to be adequate in describing the drying process for most agricultural products. The drying process is assumed to be isothermal implying that heat transfer occurs very quickly. The moisture transfer during drying often involves diffusion within the food matrix and evaporation to the gas phase. High moisture foods such as fruits are known to demonstrate two distinct drying periods. The first period is represented by a constant-rate of drying where the process is limited by the rate of evaporation of moisture from the surface. This is followed by a falling-rate period where the controlling mechanism to moisture loss is an internal mass transfer through the fruit. Evaporation of moisture into the drying air is usually dependent on the drying conditions (i.e., temperature, humidity and velocity). Drying models based on two drying periods (i.e., constant and falling) are often adequate. However, most of the models reported in the literature are limited to describing only a single period of drying (the so-called
falling-rate). There is very little information of incorporating the constant-rate period in describing the drying process.

In contrast to the constant-rate period, a vast volume of literature on modelling of the falling-rate period can be found. The falling-rate period is postulated to be controlled by the internal diffusion of moisture. Diffusion of moisture through the food matrix is a more complex process in which several mechanisms may be at play. The use of diffusion-based theories for describing the falling-rate period of drying is fairly popular because of their simplicity. The most widely investigated theoretical model in describing the drying of various foods is given by the solution of Fick's second law of diffusion using moisture concentration gradient as driving force. It is assumed that during the internally controlled process, moisture is transferred mainly by molecular diffusion. The mass transport characteristics are lumped into a single factor an "effective diffusion coefficient" which can be determined experimentally. An analytical solution to the diffusion equation is obtained if shrinkage of the material is considered negligible and that the diffusion coefficient is constant. However, it is well known that biological materials may undergo considerable shrinkage during drying. In the case of high moisture foodstuffs, a significant shrinkage has been observed. Under these circumstances, a microscopic mass balance is usually employed in the modelling of this process and numerical techniques are used for solving the moving boundary problem.

A considerable number of mathematical models based on diffusion theory have been reported to describe the drying characteristics of biological material in general. Much of this work has been done particularly on cereal grain drying. For instance, Steffe and Singh considered a spherical coordinate consisting of a composite body as a representative of rough rice, and solved an unsteady diffusion equation numerically. Thin-layer drying of corn was simulated by means of diffusional model based on Fick's second law for diffusion of sphere with constant diffusivity. Such methodology has also been successfully used to model the drying behaviour of sorghum. Ece and Cihan adopted the analytical solution of the unsteady diffusion equation in modelling the drying behaviour of rice grain. An analytical solution of the unsteady liquid
diffusion equation for rough rice drying has also been reported by Aguerre et al.\textsuperscript{133} Diffusive models were also considered to describe the convective drying of fruits and vegetables. For example, Simal et al\textsuperscript{79} used a diffusional model with moving boundary for simulating moisture movement in grapes. Simal et al\textsuperscript{78} also embraced Fick's second law of diffusion to model the drying process of green peas in both fixed and moving boundary problems. The mass transfer during drying of green beans was modelled by Rosello et al\textsuperscript{121} using both the analytical and numerical solutions to the diffusion equation.

A number of studies have also sought to model the drying process of prunes. Bertin et al\textsuperscript{134} employed optimisation techniques to estimate the unknown functions in a 'characteristic drying curve' model to describe the falling-rate period of drying plums. Weitz et al\textsuperscript{135} presented a model on the solar drying of plums based on moisture transfer analysis (Luikov's theory of drying). Techasena et al\textsuperscript{136} considered an exponential model to describe thin layer drying of plums. This model together with the heat and mass balances equations for air and product were used to simulate the drying of plums in deep bed. Most recently, Newman et al\textsuperscript{75} used a simple first-order kinetics model to describe the drying process of plums.

The above reviews of various drying models particularly on fruits exemplified the importance of modelling. However, many of these models are not necessarily valid for all kinds of food and in all moisture ranges because of the natural differences in composition of the material and the processing conditions employed. In the prune industry where almost 25\% of the energy costs account for the drying process the development of a model that would lead to an efficient operation would have great economic implications.

One of the major objectives of this research was to develop simple and realistic models capable of describing the entire drying process of plums and to examine their applicability under a range of drying conditions. For this purpose, two different mathematical models were formulated and tested against the experimental drying data.
This chapter presents the development and validation of the two proposed models and their relevance to interpreting the mechanisms involved in the drying of plums.

3.2 TWO-REGIME DRYING MODEL

3.2.1 Model Formulation

A mathematical model embracing the two regimes of drying is adopted here to describe the drying behaviour of plums. The experimental drying data were tested against a simple two-regime model which shows that the dehydration of prunes may be represented by two distinct periods of drying with different controlling mechanisms namely an evaporation controlled regime followed by a period where migration through the fruit limits the drying rate.

The two-regime drying model is a special case of the so-called generalised order kinetics, which assumes a combination of two or more periods of drying. The model was formulated by considering that the rate of moisture loss is proportional to the instantaneous moisture concentration gradient raised to some power. The power represents the order of reaction which describes the drying periods and $K$ (generalised rate constant) is a proportionality factor.

$$\frac{dW}{dt} = K (W_e - W)^n$$

(1)

where:

- $\frac{dW}{dt}$ = drying rate (kg/s)
- $K$ = generalised rate constant ($s^{-1}$)
- $W_e$ = final equilibrium mass loss (kg)
- $W$ = mass loss at any time $t$ (kg)
- $n$ = order of reaction

Most drying processes for materials with high moisture contents usually can be divided into two or more distinct periods. The prune is particularly suited to such analysis as it initially has very high moisture content. The model then assumes the
combination of these periods to describe the entire drying process for plums. During the first period of drying there is plenty of moisture available near the surface and consequently the drying rate might be expected to be a constant. This is limited by the evaporation rate of water from the surface because the moisture movement within the fruit is rapid enough to maintain a saturated condition at the surface. The constant-rate period is usually found for high-moisture foodstuffs and depends mainly on the characteristics of the drying air surrounding the product. As moisture near the surface is depleted, a concentration gradient is created within the fruit. This results in a falling rate of drying. During the falling-rate period, the transport of water within the fruit is the controlling mechanism and that the driving force is predominantly governed by the gradient of moisture content and (perhaps) temperature gradient. Usually any preliminary pre-heating period when the cold plums are rapidly reaching the oven temperature is very short compared to overall drying time and in practice can be neglected. The validity of ignoring the preheating period may be verified by carrying out experiments looking at the fruit temperature profile. Raising the temperature of the plum to a stable value ($T_s$), from an initial fruit temperature ($T_i$) at room conditions was a rapid process under the current experimental conditions. The model ignores shrinkage of the plum during drying and assumes no change in the surface area occurs.

A solution to equation 1 with $n=0$ (zero order kinetics) was used to evaluate the constant rate period. Sokhansanj and colleagues have given the fundamental equation in this period.

$$\frac{dW}{dt}_c = \frac{hA(T_a-T_s)}{H_v} \quad (2)$$

where:

- $(dW/dt)_c$ = drying rate at constant-rate period (kg/s)
- $h$ = apparent heat transfer coefficient (Wm$^{-2}$ K$^{-1}$)
- $A$ = area of heat transfer (m$^2$)
- $T_a$ = dry-bulb temperature of the drying air (K)
- $T_s$ = stable fruit temperature during constant period (K)
- $H_v$ = latent heat of vaporisation (J/kg)
This part of the process is limited by the boundary condition (W=0 to W=W_{cr}). The moisture content at the junction of the constant-rate period and the falling-rate period is termed as the critical moisture content (W_{cr}). This point marks the end of the constant-rate period and signifies the start of the drying process during which the rate of moisture movement within the fruit controls the process. The critical moisture content is usually a dependent on particle size and on the condition of the drying air. Complexity of the material structure however creates difficulties in establishing this point. The most reliable method of determining this value is by an experiment performed under similar conditions to those employed in industrial practice.

The moisture loss profile of the falling-rate period where the rate of drying is limited by the rate of diffusion of moisture within the fruit matrix can be described by first-order kinetics (n=1). In this case only a single phase of falling-rate period was considered.

\[ \frac{dW}{dt} = k(W_e - W) \]  \hspace{1cm} (3)

At the critical point, which is the boundary between the two periods, the generalised rate constant (K) in eqn.(1) can be calculated from eqn.(2) and eqn.(3), applying the boundary conditions (W=W_{cr} to W=W_e) and assuming a continuous process.

\[ K = \frac{hA(T_a-T_s)}{H_v(W_e-W_{cr})} \]  \hspace{1cm} (4)

The proposed model uses equations (1) - (4) to predict the entire drying of plums.

3.2.2 Estimation of Model Parameters

There are various parameters that are required in order to utilise the model. The properties that were experimentally determined and other relationships that were found from literature are discussed below.

In order to estimate the critical mass loss (W_{cr}), a fruit temperature profile as a function of time under particular conditions is needed. This allows estimation of the drying time (t_{cr}) and mass loss (W_{cr}) at critical point and the stable fruit temperature (T_s) during
constant-rate period of drying to be made by regression analysis. At the critical point, the fruit temperature starts to increase from its constant value due to increase heating within the fruit because of moisture depletion at the surface.\textsuperscript{57}

The fruit temperature profiles also enable an estimation of the average apparent heat transfer coefficient (h) to be made. It is assumed that there is no significant temperature gradient within the fruit, and that heat transfer occurs by convection between the air and the plum and conduction within the fruit. This may be verified by monitoring experimentally the surface and centre temperature profiles. Although a small temperature gradient exists at the start of heating, it is always insignificant for most of the constant drying period and can be safely neglected. The energy transmitted to the fruit by the stream of warming air estimated by Newton's law of cooling can be equated to the energy change in the fruit. Thus, the heat transfer coefficients can be estimated by developing transient equations from an overall energy balance on the fruit.\textsuperscript{140}

\begin{equation}
    hA(T_a - T) = MC_p \frac{dT}{dt} \tag{5}
\end{equation}

where $M$ is the mass of plum and $\frac{dT}{dt}$ is the fruit temperature versus time gradient. This equation may be solved by integration, applying an initial condition ($t=0$, $T=T_i$) to yield:

\begin{equation}
    \ln(T_a - T) = \ln (T_a - T_i) - \left[\frac{(hA)}{(MC_p)}\right]t \tag{6}
\end{equation}

By plotting the experimental data using the above relationship between the initial fruit temperature ($T_i$) at room conditions and the stable fruit temperature ($T_s$) during constant period, an average apparent heat transfer coefficient (h) can be evaluated from the slope by regression analysis.

\begin{equation}
    h = -\left(\text{Slope} \times M \times C_p\right)/A \tag{7}
\end{equation}

The mass loss at equilibrium ($W_e$) in equation 1 is the final limiting mass reached under particular constant drying conditions. Henderson's equation\textsuperscript{141}, which describes this relationship, can be used to estimate the $W_e$. 
1 - \( \text{Rh} = e^{-cT(MC_{edb})^n} \)  

where \( \text{Rh} \) is the relative humidity expressed as fraction, \( MC_{edb} \) is the equilibrium moisture content of the fruit (% dry basis), \( T \) is the drying temperature in °R (= °C\times1.8 + 491.67), and \( c \) & \( n \) are empirical constants. The best literature values of \( c \) and \( n \) for plums are \( 1.25 \times 10^{-4} \) and \( 0.865 \), respectively.\(^{141}\) The equilibrium or maximum mass loss (\( W_e \)) is related to the final (equilibrium) moisture content (\( MC_{edb} \)) in the following relationship.

\[
W_e = MC_{iwb} - MC_{ewb}
\]  

where \( MC_{iwb} \) is the initial moisture content of the plum in % wet basis and \( MC_{ewb} \) is equilibrium moisture content in % expressed on wet basis, given by:

\[
MC_{ewb} = \frac{100 \times MC_{edb}}{100 + MC_{edb}}
\]  

The specific heat (\( C_p \)) of plum used in equations (5-7) was determined using data by Hallstrom et al.\(^{68}\) These workers developed the following empirical relationship of \( C_p \) for fruits and vegetables of moisture content greater than 50% wet basis as a function of initial moisture content [\( C_p = (1.67 + 2.5 \times (MC_{iwb}/100)] \) (kJ kg\(^{-1}\) K\(^{-1}\)).

The average surface area of the plum (\( A \)) was approximated using an equation for a prolate spheroid particle (solid formed by the rotation of an ellipse about its major axis) given by Mohsenin.\(^6\)

\[
A = 2\pi \times b^2 + \frac{(2\pi \times a \times b)}{e} \sin e
\]

where;

\[
e = \sqrt{1-(b/a)^2} \quad \text{(eccentricity)}
\]

\[
a = \text{major semi-axis}
\]

\[
b = \text{minor semi-axis}
\]
By taking direct measurements of the plums using a micrometer the average axial dimensions were found to be about 2 cm (major semi-axis) and 1.5 cm (minor semi-axis), respectively.

The best relationship for latent heat of vaporisation used in equation 2 is \( H_v = [2501.6 - 2.275 T_s - 0.0018 T_s^2] \) (kJ/kg) given by Lydersen.\(^{142}\)

Using the above information, a computer program written in Turbo Pascal Version 7 was used to predict the mass loss and drying rate profiles. A listing of the program is presented on an enclosed disk.

### 3.2.3 Results of the Estimation of Model Parameters

In order to determine the parameters needed in the model, measurements of fruit temperature as a function of time under each drying condition were made. An iron-constantan thermocouple was used to monitor the fruit temperature profile during drying. The instrumentation outlined in the previous chapter for measuring the fruit temperature versus time was employed. In this study, the fruit surface and centre temperature profiles were monitored simultaneously. This was necessary to establish the difference between the temperature at the centre of the fruit and its surface in order to ascertain the validity of assuming negligible temperature gradient within the fruit matrix. Temperature measurements at the centre of the fruit and its surface were carried out by inserting two thermocouples into a plum sample, one into the flesh adjacent to the stone and the other as close to the fruit surface as possible without exposing the thermocouple.

Figures 3.1 shows a representative example of centre and surface temperature profiles of plums dried at conditions of 70°C temperature, 3% relative humidity and 1 m/s velocity. The data in each fruit temperature profile were the average of two replicates. Analysis of the recorded data indicates that the difference between the fruit centre and surface temperatures was never more than 1°C at the plateau region (constant period) and diminished to give identical values for virtually all the drying period. Although small temperature gradients existed at the very beginning of the runs, it was always no more
than 4°C for a very short period of time (about 5-10 minutes) and can be neglected safely. This warrants the assumption of negligible temperature gradient within the fruit matrix during the entire drying period.

![Temperature profile graph](image)

**Figure 3.1.** Surface and centre temperature profiles of plums during drying (T=70°C; Rh=3%; V=1m/s; MC_{wb}=69%).

According to Parry\textsuperscript{76} the effect of temperature gradients on moisture diffusion only becomes significant in conduction drying where intensive heating methods such as dielectric or microwave drying are employed. Thermal diffusion is usually assumed negligible in normal convective drying. Because of the small difference, the centre and surface temperatures of the fruit were averaged and the values used for subsequent analysis.

The average fruit temperature profiles of plums during drying at different levels of relative humidity of the drying air are shown in Figure 3.2. Figure 3.3 plots the plum temperature versus time during drying at various temperatures. In all cases the standard deviation of fruit temperature for two determinations was in the range of 0.1-1.5°C (ignoring the initial 15-30 minutes). These plots have similar distinct features. A sudden
Figure 3.2. Plum temperature profile during drying at different relative humidity conditions (T=70°C; V=1m/s; MC_{iwb}=69%).

Figure 3.3. Plum temperature profile during drying at different drying air temperatures (Rh=3%; V=1m/s; MC_{iwb}=69%).
increase in fruit temperature from its initial condition was exhibited at the very beginning of the drying process. The initial heating reached a near plateau region by about 15-30 minutes. After the preheating stage, the fruit temperature approximately leveled off for a certain period. It can be seen from Figure 3.3 that at higher temperatures the plateau region became shorter. In all instances the region of constant fruit temperature is followed by a small but definite increase. It is from this classical behaviour of the fruit temperature that allows the estimation of most of the parameters needed in the model.

Calculation of the apparent heat transfer coefficient \( (h) \) was carried out using the preheating period of the fruit temperature profile. This was done by plotting the natural logarithm of the difference between the temperature of the drying air and the change in average fruit temperature during the preheating period against time (equation 6). The preheating process is defined as the period of raising the fruit temperature from initial \( (T_i) \) to a stable value \( (T_s) \). Under the current experimental drying conditions the preheating period was very rapid and it took less than 10-30 minutes. Because of the observed small thermal gradient within the fruit during this period the measured fruit centre and surface temperatures were averaged to account for this difference. The experimental fruit temperature data were then fitted with a linear plot. The slope obtained from linear regression was used to estimate the apparent heat transfer coefficient \( (h) \) using equation 7 in the previous section. A typical example of the plot is shown in Figure 3.4. The linear function gave a very good fit to the experimental data.

The observed plateau region of the fruit temperature profile gives an indication of the occurrence of the constant-period of drying. According to Strumillo and Kudra\textsuperscript{57}, during this period the fruit temperature should remain approximately constant because the fruit surface (for plums this part is assumed just beneath the waxy skin layer) is saturated with moisture and that the heat supplied by the drying air is mostly used for evaporation of this moisture. It is this period that the stable fruit temperature \( (T_s) \) for each condition was estimated. The average stable fruit temperature \( (T_s) \) was determined between the points when the fruit temperature started to equilibrate after the initial heating stage to the point when it started to increase from the constant pattern. When all the free water near the fruit surface has evaporated, the fruit temperature rises again because heat
Figure 3.4. Typical plot of ln (T_a-T) versus time for the estimation of heat transfer coefficient (h) at different drying temperatures using fruit surface temperature (Rh=3%; V=1m/s; MC_{iwb}=69%).

Figure 3.5. Plum centre temperature profile during drying at 90°C (Rh=3%; V=1m/s; MC_{iwb}=69%).
losses due to evaporation decrease. From Figures 3.2 and 3.3 for instance, the point when the fruit temperature started to increase from constant value is quite noticeable. Although at elevated temperatures this point is quite difficult to identify but by magnifying portion of the fruit temperature profile, one can clearly see an approximate short constant trend (Figure 3.5). The point when the fruit temperature started to increase corresponded to the critical point which signified the end of constant-rate period and the start of falling-rate period. This junction gives further evidence that a two regime drying process is taking place.

The point that defines the boundary between the two distinct periods of drying was estimated by regression of the portions of the fruit temperature data. The plateau portion of the data was usually fitted with a linear function whilst the later part was fitted with either linear or polynomial functions where indicated. Intersection of these lines was determined to estimate the time corresponding to the critical moisture ($t_{cr}$) where the fruit temperature started to rise beyond the plateau. An illustrative example of the estimation of the critical point using this approach is shown in Figure 3.6.

![Graph showing pre-heating, constant-rate, and falling-rate periods](image)

**Figure 3.6.** Illustrative example of the plot for the estimation of critical point ($T=70^\circ\text{C}; \ Rh=28\%; V=1\text{m/s}; MC_{iwb}=69\%)$. 
From the estimated critical point, the critical mass loss ($W_{cr}$) was approximated by multiplying the $t_{cr}$ value to its corresponding drying rate at constant period for each drying condition.

It is also essential to obtain the mass loss equilibrium values associated with the given set of temperature and relative humidity for the use of the proposed model. Samples were dried continuously until a constant mass is recorded to obtain the experimental equilibrium mass loss ($W_e$) for each condition. The results revealed that the experimental mass loss exceeded beyond the initial moisture content particularly at the highest temperature studied which could due to other matter losses through the decomposition of organic compounds, in particular the sugars. This is discussed further later. This necessitates using the established empirical equation proposed by Henderson and Perry\textsuperscript{141} in estimating $W_e$.

| Table 3.1. Estimated model parameters for the proposed two-regime model. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| **Model Parameters** | **Drying condition** | **70°C** | **70°C** | **70°C** | **80°C** | **90°C** |
| Rh               | 62.36 (±0.16)   | 63.57 (±0.30)   | 64.66 (±0.30)   | 66.45 (±0.05)   | 67.36 (±0.24)   |
| $T_s$            | 22.38 (±1.02)   | 23.85 (±3.88)   | 24.92 (±1.23)   | 22.18 (±1.18)   | 19.76 (±1.80)   |
| h                | 7.24 (±0.02)    | 8.34 (±0.11)    | 10.31 (±0.13)   | 2.29 (±0.43)    | 1.17 (±0.19)    |
| $t_{cr}$         | 34.63 (±0.96)   | 35.69 (±4.61)   | 38.39 (±1.72)   | 19.24 (±2.55)   | 14.56 (±1.26)   |
| $W_{cr}$         | 68.68 (±0.04)   | 63.92 (±0.65)   | 59.11 (±0.45)   | 68.94 (±0.04)   | 68.95 (±0.01)   |
| $W_e$            | 0.14 (±0.01)    | 0.16 (±0.04)    | 0.18 (±0.02)    | 0.17 (±0.00)    | 0.23 (±0.01)    |
| K                | 0.14 (±0.01)    | 0.16 (±0.04)    | 0.18 (±0.02)    | 0.17 (±0.00)    | 0.23 (±0.01)    |

where:

- $Rh =$ relative humidity (%)  
- $T_s =$ stable fruit temperature (°C)  
- $h =$ heat transfer coefficient (W/m\textsuperscript{2}K)  
- $t_{cr} =$ drying at critical point (h)  
- $W_{cr} =$ mass loss at critical point (%)  
- $W_e =$ mass loss at equilibrium (%)  
- $K =$ generalised rate constant (K\textsuperscript{-1})
The estimated model parameters under the different drying conditions studied are summarised in Table 3.1. These are average quantities derived from the fruit temperature data between the surface and the centre. The errors shown in the table are the standard deviations of the values determined between the fruit surface and centre temperatures. Temperature values in each surface and centre profile were the average of two independent measurements. The values of the apparent heat transfer coefficients (h) were about 19-25 Wm\(^{-2}\) K\(^{-1}\). This is consistent with values from the literature.\(^68, 143, 144\) These authors showed that the heat transfer coefficient values were in the range of 20-30 Wm\(^{-2}\)K\(^{-1}\) for convective air drying of solid foodstuffs particularly fruits and vegetables.

The results show that the apparent heat transfer coefficient (h) increased with increase in relative humidity of the drying air. This behaviour indicates that the plums exposed to drying air of high humidity are more likely to experience intense heating compared to those subjected at lower humidity condition assuming identical drying air temperature. Further evidence for this phenomenon can be observed from the resulting stable fruit temperature (T\(_s\)) as illustrated in Figure 3.3. Also, from Table 1 the T\(_s\) value for higher relative humidity was greater than at lower relative humidity although the difference is not more than 3°C. For example, at 3% humidity the T\(_s\) value was about 62.4°C whilst at 46% humidity the T\(_s\) was about 64.7°C. This is consistent with those reported in the literature. Lamberg\(^100\) observed higher product temperature with humidified air (49% relative humidity) than with dry air (3% relative humidity) during drying of potato at 60°C. The trend is also in agreement with what has been found in other studies.\(^143, 145\)

The observed difference in T\(_s\) values between relative humidity conditions may be explained by the difference in the initial drying rate. According to equation 1 of the proposed model the maximum rate of moisture loss during the early period of drying (constant-rate) is governed by the difference between T\(_a\)-T\(_s\) where T\(_a\) is the temperature of the drying air, constant in these cases. Thus an increase in T\(_s\) value would consequently reduce the initial drying rate. Accordingly, as the drying air relative humidity increases so the concentration gradient between the fruit and the air is decreased. This might be expected to decrease the rate of evaporation. The lower the rate of evaporation the smaller the heat loss from the fruit surfaces due to latent heat. This in turn results in a higher stable fruit temperature (T\(_s\)) during the constant period of
drying. Because the drying time is normally longer under higher humidity conditions, this can have some implications for heat-sensitive materials. It would appear that the prunes are experiencing much higher temperatures for a longer time under higher humidity conditions compared to those exposed to the same temperature but at lower humidity. It should be noted that for fruits like plums other undesirable reactions such Maillard and caramelisation might be at play particularly at higher temperature and extended drying times.

The estimated heat transfer coefficient was also found to vary with drying temperatures. It appears that raising the drying temperature would tend to decrease the heat transfer coefficient. At lower drying temperature there is likely to be increased moisture in a boundary layer. It should be noted that the thermal conductivity of the fruit is dependent on the moisture content. Drier flesh at the boundary layer will conduct less than moister flesh and result in a decreased heat transfer coefficient. Alternatively, increasing the drying temperature would tend to increase the thermal gradient between the drying air and the fruit. From the plot of ln (T_a-T) versus time (equation 6) it is indicative that the greater the thermal gradient the smaller the slope of the fitted straight line.

The values obtained for the time at critical point (t_cr) showed an increasing trend with relative humidity and decreased as the drying air temperature was increased. These phenomena suggest that the occurrence of two regimes of drying is a function of drying conditions. Clearly, increasing the moisture content of the drying air and reducing its temperature lengthen the constant period. For instance, the critical point at 70°C (lower humidity) is at 7.24 h whilst at 70°C (high humidity) and 90°C (lower humidity) it occurs at 10.31 h and 1.17 h, respectively. At elevated temperature, the critical point is difficult to define. It is also indicative from the results that the mass loss corresponding to that at the critical point (W_cr) has the largest uncertainties than that for other estimated parameters. This is because W_cr is dependent upon the combined errors from the estimation of the time at critical point (t_cr), stable fruit temperature (T_s), and the heat transfer coefficient (h). The critical mass loss (W_cr) at the end of constant-rate period has been found to vary from 14.6% to 38.4%. It was noted that W_cr decreases with decreased in relative humidity and with increased in temperature. This is consistent with the
increase in drying rate. According to Perry et al\textsuperscript{56} the critical moisture content increases with increased drying rate which means a decrease in $W_{cr}$ with increased in drying rate.

It is also worthwhile noticing that the value of the generalised rate constant ($K$) is also a function of $h$, $T_s$, $W_{cr}$ and $W_e$ parameters. The precision in the estimation of these parameters would therefore greatly affect the predicted drying curve. However, the results in general indicate that the approach of using the fruit temperature profile to estimate the abovementioned model parameters may be appropriate despite some uncertainties in the measured fruit temperatures. This gives some confidence that the two-regime model is realistic in the case of plum drying and that it is possible to obtain reasonable estimates of most of the parameters needed for the model from the fruit temperature profile during drying.

### 3.2.4 Evaluation of the Two-Regime Model

Before testing the experimental data with the proposed two-regime model, preliminary investigations were made to assess the drying behaviour of plums. This was done by initially fitting the entire drying curve with a simple first-order kinetic model (equation 3). The first-order kinetics model has been used for describing the drying kinetics of various fruits and vegetables.\textsuperscript{146, 147} More recently this model was used by Newman et al\textsuperscript{75} for representing the drying kinetics of prunes and found to work reasonably well.

Integrating equation 3 with the boundary condition ($W=W_o=0$ to $W=W$) would yield;

\[
\ln(W_e-W) = \ln(W_e) - kt
\]

where $W_e$ and $W$ are the mass losses of the plum at equilibrium and after drying time $t$, respectively. By plotting the experimental data $\ln (W_e-W)$ versus time from $W=0$ to $W=62.8\%$ (which is equivalent to 20\% moisture content in dry basis) the rate constant ($k$) for each condition was determined from the slope of the line. An illustrative example of this plot is shown in Figure 3.7. It can be observed that the linear approximation to the experimental data becomes inadequate as the temperature is decreased.
Figure 3.7. Plots for the moisture loss during drying of plums at different temperatures expressed as a first-order rate process (Rh=3%; V=1m/s; MC_{wb}=69%).

The rate constant (k) is related to temperature by Arrhenius equation \[ k = k_0 \exp(-\frac{E_a}{RT}) \]. The activation energy (E_a) in J/mol was estimated from the slope (which is the ratio of activation energy and the gas constant) of a semi-log plot of the rate constant (k) versus inverse absolute temperature (1/T) taking the gas constant (R) value of about 8.314 J/mol K. Figure 3.8 shows the Arrhenius plot of the data. The figure illustrates a good linear fit to the data in the range of 70-90°C with an activation energy of about 36 kJ/mol whilst the value at 60°C was found to deviate from the trend. The activation energy at 60-70°C range was observed to be about 86 kJ/mol. The lack of good linear approximation at 60°C as seen in Figure 3.7 results in a large uncertainty in E_a at lower temperature. However, in general the estimated activation energy values for plums are similar to those obtained by other authors for different products: 31-80 kJ/mol in prune; 43 kJ/mol in raisins; 33-37 kJ/mol in grapes; 28 kJ/mol in green peas. The observed higher activation energy at 60-70°C may suggest that the water loss process is more hindered at this condition and hence requires more energy to mobilise the water molecules. This is consistent with the suggestion of poor efficiency of cell
disruption particularly at the waxy skin layer under this condition as discussed in chapter 2.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3_8.png}
\caption{Temperature dependence of rate of plum drying in terms of Arrhenius plot  
(Rh=3%; V=1m/s; MC_{iwb}=69%).}
\end{figure}

Figure 3.9 shows an illustrative example of the comparison between the experimental mass loss data and the predicted values using the simple first-order kinetics model. It is seen that there was very poor agreement during the early stages of drying and a tendency to conform at the later part of the process. It was noted that at elevated drying temperature the discrepancy between the experimental and the predicted values at the early stages of drying is small but an increasing disagreement emerged at the later stages. This implies that the mechanism of moisture loss is likely different at various stages of the drying process of plums and may be dependent upon the drying conditions. The two-regime drying model should address this shortcoming.

In the course of drying plums, water moves from the interior of the fruit to the skin layer, diffuses through the skin layer and emerges at the outer surface from which it is removed by the drying air. It is this concept that a model was formulated to describe the
drying kinetics of plums. The proposed two-regime model was tested against the kinetics of plums dried at different levels of relative humidity of the drying air. This particular set of data was first selected because it was initially found (by initial inspection of the curve) to exhibit two distinct periods of drying. Using the parameters shown in Table 1 under these conditions, the drying kinetics of plums at different relative humidity conditions were simulated. Figure 3.10 depicts the experimental mass loss and the corresponding values predicted from the two-regime drying model.

It can be seen from this figure that the experimental mass loss values were predicted well particularly at lower humidity conditions where fluctuations of humidity were minimal. At higher humidity conditions the problem of fluctuations in the drying air humidity causes some systematic discrepancies. The experimental data show that at the highest humidity studied the maximum deviation of relative humidity was as much as $\pm 3\%$. However, these conditions in general exhibit a good agreement between the experimental data and the model curve for majority of the entire drying period. The experimental data also show that there was a small increase in the mass (about 1.4%)
Chapter 3

during the first few minutes of drying which could be due to condensation of moisture from humid air on the fruit surface. This was more prominent at higher relative humidity conditions. The observed slight delay in drying may be also attributed to the initial heating period due to thermal equilibration. This phenomenon, however, was not included in the model, resulting in the predicted initial mass loss slightly deviating from the experimental values.

![Figure 3.10](image.png)

**Figure 3.10.** Comparison between the experimental mass loss data and the predicted values at different relative humidity conditions (T=70°C; V=1m/s; MC\textsubscript{w}=69%).

From the results, it may be concluded that at 70°C temperature the two regime model fits the experimental data at low relative humidity condition extremely well, and reasonably well at higher relative humidities and would be a useful predictive tool for these conditions. In addition, ignoring the very short preheating period had little effect on the overall quality of the fits to the experimental data.

To ascertain the significance of the two regimes of drying at various conditions, the proposed model was tested against the experimental data obtained at different drying air temperatures. Model parameters estimated under these conditions are also shown in
Table 3.1. It can be seen that the temperature gradient between the drying air and the fruit \((T_a - T_s)\) increased with drying temperature. This primarily accounts for the significant difference in the initial drying rate between temperatures. There was a decreasing trend of heat transfer coefficient \((h)\) as the drying air temperature is increased but this was offset from the large temperature gradient between the drying air and the fruit. For instance, at 70°C the temperature difference between the drying air and the fruit was about 7.6°C whilst at 90°C this difference was 22.6°C. Correspondingly, the heat transfer coefficient \((h)\) was just reduced to around 2.6 W/m²K from 70°C to 90°C. It should be noted that both parameters (heat transfer coefficient & temperature gradient) are directly proportional to the initial drying rate as manifested in equation 2. The evaporative cooling effect could be possibly the reason for maintaining the relatively lower stable fruit temperature \((T_s)\) compared to the drying temperature. The other fact could be attributed to the amount of heat dissipated during the drying process. At a higher drying rate, for instance, more heat is consumed due to greater rate of moisture evaporation hence less residual heat is transmitted to the fruit. It was also found that the stable fruit temperature \((T_s)\) was short lived at elevated temperature. This is confirmed in Figure 3.3 and in the estimated \(t_{cr}\) values shown in Table 3.1. The result indicates that the constant-rate of drying becomes negligible as the temperature is increased.

Figure 3.11 shows the mass loss profile of the plums during drying at different temperatures together with the predicted results of the two-regime model. An extremely good fit to the experimental mass loss was found at 70°C over the entire drying period. For higher temperatures, the predicted curves deviated from the experimental mass loss curves at longer drying times. At 90°C, the gap between the experimental and the predicted values in the early part of falling-rate period (approximately after 3-5 hours) was greater. Particularly at the highest temperature, the deviations between the model and the experiment especially at longer drying times may be ascribed to the fact that there might be two or more falling-rate periods of drying. It should be emphasized that the proposed model describes the entire falling-rate regime by a single period. The model would therefore appear to be limited in depicting the falling-rate period of drying at higher drying temperatures. Other possible reasons are that at higher temperatures the constant-rate period may not relevant and that the effect of assuming no water loss
during the pre-heating period may be inadequate. Uncertainties in the estimation of the critical point might have been also contributed to the observed discrepancies between the experimental and predicted values.

The theory of the model suggests that the parameters estimated from the critical point such as \( t_{cr} \) and \( W_{cr} \) do not directly affect the constant-rate period (although the critical point might have some small impact on the \( T_s \) values) but are of great influence to the predicted falling-rate period. From the integrated form of equation 3 (boundary condition: \( W=W_{cr} \) to \( W=W_e \)) there is a tendency of a compounding effect of the error in the estimation of critical point the fact that \( t_{cr} \) and \( W_{cr} \) derived from the estimation of this point are associated to the predicted mass loss (\( W \)) within this boundary. These consequently contributed to some uncertainties of the predicted results.

In order to assess further the drying behaviour of the plums as well as the predictive potential of the two-regime model it was necessary to plot the experimental data and predicted results in terms of drying rate versus time. This approach allows one to clearly

**Figure 3.11.** Comparison between the experimental mass loss data and the predicted values at different drying air temperatures (\( Rh=3\% \); \( V=1\text{m/s} \); \( MC_{iwb}=69\% \)).
characterise the drying behaviour. The experimental drying rates were approximated from the mass loss data using the method described in the previous chapter whilst the predicted drying rates were directly estimated by the model. Figure 3.12 shows replots of the data for three different drying temperatures derived from mass loss data together with the results from the model in terms of drying rate versus time. At the lowest temperature studied, there are clearly two distinct regimes of drying (neglecting the initial 15-30 minutes where equilibration of fruit temperature is taking place). This was also observed by Karathanos and Belessiotis\textsuperscript{149} who studied the kinetics of drying plums at 70°C with relative humidity of 12% and air velocity of 1 m/s. The early stages of drying in general can be approximated by a constant-rate period whilst the later part of drying by a falling-rate period. At 70°C temperature, the concept of two regimes of drying fits well to the experimental data. The proposed model produced reasonable agreement between the predicted and experimental values for the drying of plums during both major drying periods.

Figure 3.12. Comparison between the experimental drying rate and the predicted values at different drying air temperatures (Rh=3%; V=1 m/s; MC\textsubscript{iwb}=69%).
At higher temperatures, the falling-rate regime dominates the entire drying process. Hence the approximation of a constant rate in the early part of the drying process for higher temperatures seems not plausible resulting in a poorer prediction of drying. Obviously, at higher temperatures the rate of moisture loss is very rapid and water depletion near the surface occurs quickly. This means that the rate of moisture diffusion within the fruit matrix is not enough to replenish the fast evaporation of moisture from the fruit surface to the drying medium. It can also be seen from the figure particularly at 90°C that there was initially greater difference between the predicted and the experimental drying rates. This further suggests that at higher temperatures the drying behaviour in the falling-rate stage might not be following a single period. The other possible reason could be due to the explicit assumption that the fruit has a fixed volume during drying. Most foods however shrink when dried, and it was observed from this study that the plums' volume shrunk by up to 70% from their initial.

Generally, the approach appears to be a promising tool in predicting the kinetics of drying plums at moderate drying conditions and can be extended to other waxy fruits.

3.3 DIFFUSION DRYING MODEL

The two-regime model has been shown to be adequate in describing the drying process of plums under moderate drying conditions. At higher drying temperatures its validity is limited, implying that other mechanisms may be involved. It is in this context that further efforts were taken to establish an appropriate model that would describe the kinetics of drying plums under these conditions, by considering the diffusion of water through the fruit explicitly. Under extreme drying conditions particularly at higher temperatures and velocities with lower humidity conditions, the external resistance to moisture transfer is usually negligible. The entire drying process can be described by the rate at which the moisture diffuses from the interior portion to the surface. Under these circumstances, the drying process is usually modelled using Fick's law of diffusion, which states that the mass transfer mechanism is proportional to the moisture concentration gradient within the body. The solution to Fick's law of diffusion depends on the geometrical and compositional properties of the material and the nature of mass transfer resistance. In the case of drying high moisture foodstuffs like
plums, shrinkage usually occurs. This complicates the solution to the diffusion equation whilst the presence of solid stone in the plum further aggravates the situation. In this section the development and validity of a diffusion model for describing the drying process of high-moisture plums are presented and examined under different drying conditions.

### 3.3.1 Development of Diffusion Drying Model

The proposed diffusion model assumes the main driving force for mass transfer is internal moisture gradients with a symmetrical radial diffusion process.\(^{107}\) Obviously, the controlling mechanism of moisture transfer would be diffusion within the fruit matrix. Drying of plums was assumed to be an isothermal process with significant shrinkage occurring. In this case Fick’s law of diffusion was adopted to describe the moisture diffusion process. In order to account for shrinkage the moving boundary problem was solved by microscopic mass balance applying a numerical solution and using a finite difference method.\(^{79,129}\)

![Figure 3.13. Schematic diagram of the plum used for diffusion model.](image-url)
Another important consideration made in developing a diffusion drying model was that the plum viewed as a composite spherical body comprised of two concentric materials (stone and flesh) having different properties. Figure 3.13 shows the pictorial representation of a plum used for the diffusion analysis. The flesh component of the spherical plum was divided into N (maximum number of shells) concentric spherical shells surrounding a spherical core requiring the moisture content to be specified at each shell. The total number of spherical shells in the flesh component was to remain constant throughout the drying process. The spherical shells are of equal thickness ($\Delta r$) except the surface segment which was half the thickness. The radial length decreased due to shrinkage and consequently the thickness of each shell reduced as drying progresses. The reduction in radial length was equally distributed across the flesh side keeping uniform thickness of each shell in every time step. The moisture concentration was assumed to be uniform within each shell. A microscopic mass balance in each shell element was performed at the nodal point (i), which is the midpoint between the two surfaces of the shell. This was applied to all the shells for every time step ($\Delta t$) to establish the moisture content distribution in the space-time domain across the fruit. The mass balance for one shell at time $t+\Delta t$ was obtained as a function of the properties of the neighboring shells at time $t$. In the first time interval, the moisture content in each shell and the new dimension were evaluated using the initial conditions. Subsequently, the average moisture content of the flesh component of the plum was calculated by numerical integration of the moisture content in each shell over the total volume of the flesh component. In turn the average moisture content of the whole plum was estimated by taking into account both the stone and flesh components. The time interval was then determined based on the new dimension. This meant that the successive time increments were of various durations. Taking a microscopic mass balance in each shell, the difference between the amount of diffusing moisture which passes in and out through the spherical walls of the $i^{th}$ shell is equal to the moisture stored within the shell (eqn 1).

\[
\text{Accumulation} = Q_{in} - Q_{out} \quad \text{eqn (1)}
\]

where:

$Q_{in}$ = quantity of moisture flowing into the $i^{th}$ shell
Chapter 3

\[ Q_{\text{out}} = \text{quantity of moisture flowing out from the } i^{th} \text{ shell} \]

The accumulation of moisture in the \(i^{th}\) shell of the thickness \(\Delta r\) can be obtained as;

\[
\text{Accumulation} = (4 \pi r^2 \Delta r) \frac{\partial M}{\partial t} \quad \text{eqn (2)}
\]

where:
- \(r\) = radial coordinate of the \(i^{th}\) shell (m)
- \(\Delta r\) = thickness of the \(i^{th}\) shell (m)
- \(\frac{\partial M}{\partial t}\) = moisture accumulation with time in the \(i^{th}\) shell

The quantity of moisture flowing into the \(i^{th}\) shell \((Q_{\text{in}})\) is given by;

\[
Q_{\text{in}} = (-4 \pi [r-(\Delta r/2)]^2 \text{Deff}_{\text{in}} \frac{\partial M}{\partial r})_{\text{in}} \quad \text{eqn (3)}
\]

where:
- \(\text{Deff}_{\text{in}}\) = mean effective diffusivity between \((i-1)^{th}\) & \(i^{th}\) shells
- \(\frac{\partial M}{\partial r}_{\text{in}}\) = moisture profile between \((i-1)^{th}\) and \(i^{th}\) shells

while the amount of moisture flowing out of the shell \((Q_{\text{out}})\) can be expressed as;

\[
Q_{\text{out}} = (-4 \pi [r+(\Delta r/2)]^2 \text{Deff}_{\text{out}} \frac{\partial M}{\partial r})_{\text{out}} \quad \text{eqn (4)}
\]

where:
- \(\text{Deff}_{\text{out}}\) = mean effective diffusivity between \(i^{th}\) and \((i+1)^{th}\) shells
- \(\frac{\partial M}{\partial r}_{\text{out}}\) = moisture profile between \(i^{th}\) and \((i+1)^{th}\) shells

The finite difference representations of the differentials in eqns (2) - (4) are;

\[
\frac{\partial M}{\partial t} = \frac{M_{r}^{i+\Delta t} - M_{r}^{i}}{\Delta t} \quad \text{eqn (5)}
\]

\[
\frac{\partial M}{\partial r}_{\text{in}} = \frac{M_{r}^{i} - M_{r-\Delta r}^{i}}{\Delta r} \quad \text{eqn (6)}
\]

\[
\frac{\partial M}{\partial r}_{\text{out}} = \frac{M_{r+\Delta r}^{i} - M_{r}^{i}}{\Delta r} \quad \text{eqn (7)}
\]
where:
\( \Delta t = \) time increment (sec)

\( M_{r_i} = \) moisture content of the \( i^{th} \) shell at time \( t \)

\( M_{r_i+\Delta r} = \) moisture content of the \((i+1)^{th}\) shell at time \( t \)

\( M_{r_i-\Delta r} = \) moisture content of the \((i-1)^{th}\) shell at time \( t \)

\( M_{r_i+\Delta t} = \) moisture content of the \( i^{th} \) shell at time \( t+\Delta t \)

Substitution of eqns (2) - (7) into eqn (1) and simplification yields:

\[
M_{r_i+\Delta t} = M_{r_i} - \left( C_1 \left( C_2 D_{eff_i} \left( M_{r_i} - M_{r_i-\Delta r} \right) - C_3 D_{eff_0} \left( M_{r_i+\Delta r} - M_{r_i} \right) \right) \right) \quad \text{eqn (8)}
\]

where:

\[
C_1 = \frac{\Delta t}{(\Delta r^2 + r^2)}
\]

\[
C_2 = [r-(\Delta r/2)]^2
\]

\[
C_3 = [r+(\Delta r/2)]^2
\]

Equation (8) is only valid for shells within \((R_s < r < R_p)\), where \( R_s \) is the radius of the stone component while \( R_p \) is the radius of the whole plum.

At the stone-flesh interface (where \( r=R_s \)) eqn (8) is not valid due to the different material properties on the two sides. Taking a mass balance at the stone-flesh interface, the accumulation of moisture within the stone-flesh shell becomes:

\[
\text{Accumulation} = \text{Accumulation}_f + \text{Accumulation}_s \quad \text{eqn (9)}
\]

where:

\[
\text{Accumulation}_s = \text{accumulation of moisture in the stone-side} = (4 \pi r^2 \Delta t) \left( \frac{\partial M}{\partial t} \right)_{s=\text{in}}
\]

\[
\text{Accumulation}_f = \text{accumulation of moisture in the flesh-side} = (4 \pi r^2 \Delta t) \left( \frac{\partial M}{\partial t} \right)_{f=\text{out}}
\]

Assuming no moisture in the stone component, then the moisture flow \( Q_{in} \) from the stone side to the stone-flesh interface shell and the accumulation of moisture at the stone
side of the stone-flesh interface shell become zero at t=0 and t>0. Substituting eqns (4), (5), (7) & (9) into eqn (1) and simplifying yields:

$$M_r^{t+\Delta t} = M_r^t + [C_1*2*Deff_{out}*C_3^* (M_r^t - M_r^{t+\Delta t})]$$  \hspace{1cm} eqn (10)

The mass balance in the outermost shell, which had a thickness of \(\Delta r/2\) was taken on its external surface. The moisture content of the outermost shell assumed to be constant during the process is equal to equilibrium moisture content \(M_e\).\(^{79}\) Thus at any time \(t\) \((t>0)\), the moisture content \((M_r^1)\) of the \(N^{th}\) shell \((surface; r=R_p)\) becomes:

$$(M_r^1) = M_e$$  \hspace{1cm} eqn (11)

Given the initial moisture content \((M_0)\) for each point in the plum and the equilibrium moisture content \((M_e)\), the above set of equations was used to describe the moisture movement and distribution at any time thereafter. The calculations were repeated for the next time steps assuming that the initial values were the results of the previous time interval. The initial moisture content \((M_0)\) was assumed to be uniform across the flesh component of the plum. Equilibrium moisture content \((M_e)\) was estimated for each drying condition using Henderson's equation.\(^{141}\) Detailed explanation of the Henderson's equation was presented in the previous section.

The moisture content, which is normally determined during drying experiments, is an average for the entire composite body. In order to compare with the experimental values the average predicted moisture content of the whole plum was determined which is the average moisture content of two individual components (stone & flesh). The average moisture content of the flesh component at any time was estimated by numerically integrating the moisture contents of the nodal points using Simpson's rule.\(^{151}\) The average moisture content\(^{76}\) of the flesh component is represented by:

$$M_f = (1/V_f)\int_0^{R_p} 4\pi r^2 M(r) \, dr$$  \hspace{1cm} eqn (12)

where:

$$M_f = \text{average moisture content of the flesh component}$$
\( V_f = \) volume of flesh component of the plum
\[ = \frac{4}{3}\pi(R_p^3 - R_s^3) \]
\( M(r) = \) moisture content of the \( i^{th} \) nodal point at radial coordinate \( r \)

Substituting into eqn (12) and rearranging:

\[
M_f = \frac{3}{(R_p^3 - R_s^3)} \int r^2 M(r) \, dr \quad \text{eqn (13)}
\]

Integrating eqn (13) numerically using Simpson’s rule:

\[
I = \frac{(h/3)[f(x_a) + f(x_b) + 4 \sum_{j=1,3,5,\ldots,(n-1)} f(x_j) + 2 \sum_{j=2,4,6,\ldots,(n-2)} f(x_j)]}{A_i^2}
\]

where:

\[ h = \text{distance between nodal points (m)} \]
\[ = \Delta r \]
\[ f(x_i) = \text{moisture content for the } i^{th} \text{ nodal point} \]

The use of Simpson’s rule requires that an even number of shells be used in the numerical solution.151

Thus the solution to eqn (13) yields:

\[
M_f = \frac{\Delta r}{(R_p^3 - R_s^3)}[A_1 + A_2 + (4A_3) + (2A_4)] \quad \text{eqn (14)}
\]

where:

\[ A_1 = (M_i*r_i*r_i) ; i = R_p \]
\[ A_2 = (M_i*r_i*r_i) ; i = R_s \]
\[ A_3 = \sum(M_i*r_i*r_i) ; i = 1,3,5,\ldots,(N-1) \]
\[ A_4 = \sum(M_i*r_i*r_i) ; i = 2,4,6,\ldots,(N-2) \]
Therefore, the average moisture content of the whole plum ($M_p$) at every time step ($\Delta t$) is the average moisture content between the two components (stone & flesh) which is generally represented by:

$$M_p = \sum (d_{mj} * M_j) ; j = 1 \text{ to } m \quad \text{eqn (15)}$$

where:

- $d_{mj} = \text{dry matter fraction of the } j^{th} \text{ component}$
- $M_j = \text{moisture content of the } j^{th} \text{ component (kg H}_2\text{O/kg dm)}$
- $m = \text{total no. of components in the plum}$

The dimensional change during drying is an important feature of this model. In order to account for the shrinkage factor, the dimensional change of the plum was assumed to occur only in the flesh section ($R_s < r < R_p$) and that the volume of the stone component was considered to remain constant throughout the drying process. Thus the radius of the stone ($R_s$) remains constant whilst the space interval ($\Delta r$) between nodes in the flesh section and the radial coordinate ($r$) shrink as drying proceeds. Shrinkage was also assumed to be equal in all dimensions of the sphere. The shell sizes were reduced due to moisture losses while adjusting their dimension to the moving boundary. The radial coordinate and the thickness of the shell ($\Delta r$) for every time step were estimated according to the amount of moisture lost after time $t + \Delta t$. The volume of the plum after time $t+\Delta t$ was estimated from the moisture loss:

$$V = V_o - [(M_p^t - M_p^{t+\Delta t}) * d_m * (1/D_w)] \quad \text{eqn (16)}$$

where:

- $V = \text{volume of the plum at time } t+\Delta t (m^3)$
- $V_o = \text{initial volume of the plum (m}^3)$
- $M_p^t = \text{average moisture content of the plum at time } t$
- $M_p^{t+\Delta t} = \text{average moisture content of the plum at time } t+\Delta t$
- $d_m = \text{dry matter content of the plum}$
- $D_w = \text{density of water (1000 kg/m}^3)$
Then solving the radius of plum ($R_p$) for a sphere of given volume ($V$);

$$R_p = [(3*V)/(4*\pi)]^{1/3} \quad \text{eqn (17)}$$

Thus $\Delta r$ at every time step can be evaluated as;

$$\Delta r = (R_p - R_s)/(N-1) \quad \text{eqn (18)}$$

where:

$N = \text{maximum number of shells in the flesh-side}$

Also, at any time step the radial coordinate ($r$) of the $i^{th}$ shell is;

$$r_i = R_s + \Delta r (i-1) \quad \text{eqn (19)}$$

where:

$i = \text{nodal point at the center of each } i^{th} \text{ shell}$

In order for the numerical solution technique to be stable, the time and radial increment must meet certain criteria given by Gekas.143

$$\Delta t = \Delta r^2/(2*D_{eff}) \quad \text{eqn (20)}$$

From equation (20) it is obvious that the time increment ($\Delta t$) is changing every step with the moving boundary.

A computer program written in Turbo Pascal Version 7 was used to iteratively solve the above set of equations. Listing of the program can be found on the attached disk. Using this program, it was possible to estimate the moisture content distribution within the flesh component of the plum and the average moisture content of the whole plum as a function of drying time.
3.3.2 Determination of the Parameters in the Diffusion Model

The general data used for the diffusion model are shown in Table 3.2. These were determined experimentally. The average mass of the whole fresh plums was found to be about 19 grams (+ 2.6). The initial moisture content (wet basis) of the plum was around 66% (+ 1.5). This was the average of seven replications determined from the sample obtained during the 1996 season. It means that the amount of dry matter within the whole plum was about 34%. In terms of dry basis, this corresponds to moisture content of about 1.95 kg H₂O/kg dry matter for the whole plum. Details of the procedure in determining the initial moisture content are outlined in chapter 2.

Table 3.2. General data used for the diffusion model.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial volume of the plum (cm³)</td>
<td>18.00</td>
</tr>
<tr>
<td>Volume of the stone (cm³)</td>
<td>0.91</td>
</tr>
<tr>
<td>Radius of the plum (mm)</td>
<td>16.00</td>
</tr>
<tr>
<td>Radius of the stone (mm)</td>
<td>5.50</td>
</tr>
<tr>
<td>Mass of the plum (g)</td>
<td>19.91</td>
</tr>
<tr>
<td>Initial moisture content of the plum (kg H₂O/kg fresh weight)</td>
<td>0.66</td>
</tr>
<tr>
<td>Stone component (g/g fresh weight)</td>
<td>0.05</td>
</tr>
<tr>
<td>Mass of the stone component (g)</td>
<td>0.95</td>
</tr>
<tr>
<td>Mass of the flesh component (g)</td>
<td>18.06</td>
</tr>
<tr>
<td>Dry matter content of the plum (g)</td>
<td>6.45</td>
</tr>
<tr>
<td>Dry matter content of the stone component (g)</td>
<td>0.95</td>
</tr>
<tr>
<td>Dry matter content of the flesh component (g)</td>
<td>5.50</td>
</tr>
<tr>
<td>Water content of the flesh component (g)</td>
<td>12.56</td>
</tr>
<tr>
<td>Water content of the stone component (g)</td>
<td>0.00</td>
</tr>
<tr>
<td>Dry matter fraction of the stone</td>
<td>0.15</td>
</tr>
<tr>
<td>Dry matter fraction of the flesh</td>
<td>0.85</td>
</tr>
<tr>
<td>Initial moisture content of the flesh component (kg H₂O/kg dry matter)</td>
<td>2.29</td>
</tr>
<tr>
<td>Initial moisture content of the stone component (kg H₂O/kg dry matter)</td>
<td>0.00</td>
</tr>
<tr>
<td>Initial moisture content of the whole plum (kg H₂O/kg dry matter)</td>
<td>1.95</td>
</tr>
</tbody>
</table>
To account for shrinkage in the numerical solution, an equation that relates the volume or radial change to the average moisture content during drying is required. Shrinkage during drying was assumed to take place only in the flesh component of the plum and that the plum shrunk corresponding to the occupied region abandoned by water.\textsuperscript{152, 153} Using the known initial volume, the dimensional change of plum at any time during drying was estimated from the mass loss data assuming that the reduction of mass is only due to removal of water. The initial volumes of the whole plum and the stone were determined by a water displacement method.\textsuperscript{6, 79} Several researchers have estimated the change in volume during drying of grapes as equivalent to the amount of moisture removed.\textsuperscript{77, 79, 154} Vaccarezza\textsuperscript{155} proposed a volume decrease according to the space occupied by water that leaves in the product during drying of sugar beet roots.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{volume_moisture_content.png}
\caption{Changes in volume of plums during drying as a function of moisture content (T=80°C; Rh=3%; V=5m/s; MC\textsubscript{w}b=66%).}
\end{figure}

Figure 3.14 illustrates the change in volume with moisture content estimated from the moisture loss data. From the analysis of the curve, it was found that the volume of the plum reduced to about 70\% from its initial size down to the size corresponding to a moisture content of 20\% (dry basis). The figure indicates a very good linear relationship
between volume and moisture content. Several authors have reported such a dependency of volume with moisture content for similar products. Raghavan et al.\textsuperscript{156} and Masi and Riva\textsuperscript{146}, for example, found that the volume change during convective drying of grapes was linearly related to moisture content. A similar result has also been reported for drying of green beans by Rosello et al.\textsuperscript{121} Correspondingly, the radial change in plums during drying was determined according to the volume of a spherical body. Figure 3.15 shows an illustrative example of radial changes of plum with time during drying at different temperatures. The plot shows that the rate of change in radius was maximum in the early stages of drying and that varied with temperature. This is because the rate of moisture loss was at its greatest during the early stages of drying and at elevated temperatures.

![Figure 3.15.](image)

**Figure 3.15.** Radial change in plums during drying as a function of time at different drying temperatures (Rh=3%; V=5m/s; MC\textsubscript{iwb}=66%).

### 3.3.3 Estimation of the Effective Diffusion Coefficient ($D_{\text{eff}}$)

Diffusion is a process by which moisture moves from one part of the system to another as a result of concentration gradients.\textsuperscript{157} The rate at which the diffusion occurs is
usually expressed in terms of a diffusion coefficient. An independent estimation of the diffusion coefficient was made to validate the diffusion model. It should be emphasised that the diffusion coefficient obtained from this study is an effective diffusion coefficient (Deff) which represents the overall transport properties of water associated with various driving forces for mass transfer. It was assumed that the diffusion coefficient is not a function of moisture concentration. The effective diffusion coefficient was separately estimated by applying Fick’s law of diffusion equation for spherical coordinates given by Crank to the experimental drying kinetics data (average moisture content versus time) assuming that the transport of water within the fruit is due to the concentration gradient.

\[
\frac{\partial M}{\partial t} = -D_{\text{eff}}\left[(\partial^2 M/\partial r^2) + (2/r)(\partial M/\partial r)\right] \quad \text{eqn (21)}
\]

Assuming \(D_{\text{eff}}\) to be independent of the moisture content of the plum and a uniform initial moisture content of the plum with no shrinkage was taking place, the analytical solution to eqn (21) for a hollow sphere with boundary condition \((R_s < r < R_p)\) is given by Crank:

\[
MR = \left(C_1 \sum_i C_2 \exp \left[\left(-n^2 \pi^2 D_{\text{eff}} t\right)/(R_p-R_s)^2\right]\right) i = 1 \text{ to } \infty \quad \text{eqn (22)}
\]

where;

\[
C_1 = \left[\frac{6}{\pi^2 (R_p^2 + (R_p R_s) + R_s^2)}\right]
\]

\[
C_2 = \left[\left(\frac{R_p \cos(\pi n)}{n}\right) - R_s\right] \frac{1}{n^2}
\]

\[
MR = \frac{(M-M_e)}{(M_0-M_e)}
\]

For large values of \(t\) eqn (22) rapidly converges and can be reduced to the first term \((i=1)\) of the series. Thus eqn (22) becomes;

\[
\ln MR = \left[\ln (C_1 C_3)\right] - \left[\left(\pi^2 D_{\text{eff}} t\right)/(R_p-R_s)^2\right] \quad \text{eqn (23)}
\]

where:

\[
C_3 = \left(\left(R_p \cos(\pi)\right) - R_s\right)^2
\]
By plotting the natural logarithm of MR versus time using the experimental drying data, $D_{eff}$ can be determined from the slope of the straight line:

$$\text{Slope} = \left[- \frac{(\pi^2 D_{eff})}{(R_p - R_i)^2}\right]$$

**eqn (24)**

Figure 3.16 depicts the natural logarithm plots of the moisture ratio versus time curves for three sets of drying experiments conducted at different temperatures. The drying kinetics data of up to 20% moisture content (dry basis) were consistently used for the analysis. It can be seen from this figure that there was a good linear fit for the entire curve of the experimental data particularly at 80°C. This may indicate a constant $D_{eff}$ independent from moisture content. The diffusivity at high moistures has been reported to be fairly constant, and decreased as moisture decreases below approximately 20% (dry basis) for food systems. At lower temperatures, however, there were deviations of the experimental data from linearity. This was more prominent at 70°C and may indicate a complex transport mechanism during drying at these conditions. In all cases, there was always an initial curvature of the experimental plots, which corresponds to the preheating stage.

![Figure 3.16. Semi-log plots of the experimental moisture ratio (MR) against time at different drying temperatures (Rh=3%; V=5m/s; MC_{iwb}=66%).]
The temperature dependence of the diffusion coefficient is often expressed by the Arrhenius equation \[D = D_0 \exp\left(-\frac{E_a}{RT}\right)\]. The estimated \(D_{\text{eff}}\) values for different temperatures were plotted in Figure 3.17 in the form of \(\ln D_{\text{eff}}\) versus \(1/T\). The Arrhenius plot illustrates a good linear fit to the data in the range of 70-80°C. The activation energy calculated from the slope of the linear regression was about 56 kJ/mol.

![Arrhenius plot](image)

**Figure 3.17.** Arrhenius plot of the effective diffusion coefficient versus inverse absolute temperature (Rh=3%; V=5m/s; MC_{wb}=66%).

The result implies that a change in temperature will considerably affect the effective diffusion coefficient \(D_{\text{eff}}\). During the drying process there was always an initial heating period. This corresponds to an increase in temperature during which equilibration is taking place. For plum drying, this stage is about 15-30 minutes depending upon the drying temperature. In an attempt to look at the effect of the initial heating process, an effective diffusion coefficient at this stage was separately estimated. This was determined from the slope of the plot of \(\ln MR\) versus time of the preheating stage. The preheating process was identified as the period from the start of drying to the point at which the drying rate is at maximum (from the drying rate versus time curves). From the fruit temperature point of view, this corresponds to the period at which the
fruit temperature starts to stabilise from its initial value at room temperature. Then the final \( D_{\text{eff}} \) was estimated from the slope of the subsequent data in each curve of the ln MR versus time plots. The good linear plot of ln MR versus time indicates that \( D_{\text{eff}} \) is independent of moisture content and principal dimension over the range of moisture content considered.

The estimated effective diffusion coefficients (\( D_{\text{eff}} \)) are presented in Table 3.3. The \( D_{\text{eff}} \) values obtained using the drying data were in the range of 2.42 \( \times 10^{-10} \) to 8.75 \( \times 10^{-10} \) m\(^2\)/s within a temperature of 70-80°C. It was generally observed that \( D_{\text{eff}} \) increases with drying temperature. The results showed that the initial \( D_{\text{eff}} \) value was lower than the final \( D_{\text{eff}} \). It was also found that the final \( D_{\text{eff}} \) was approximately similar to the overall \( D_{\text{eff}} \).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Effective diffusion coefficient (m(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Overall(^1)</td>
</tr>
<tr>
<td>70</td>
<td>5.03 ( \times 10^{-10} )</td>
</tr>
<tr>
<td>75</td>
<td>6.14 ( \times 10^{-10} )</td>
</tr>
<tr>
<td>80</td>
<td>8.75 ( \times 10^{-10} )</td>
</tr>
</tbody>
</table>

Note:

\(^1\)estimated using the entire drying data
\(^2\)estimated using the preheating period data
\(^3\)estimated using the drying data (excluding the preheating period)

The overall \( D_{\text{eff}} \) was obtained by the same approach using the entire drying curve instead of ignoring the initial heating period. The lower values of \( D_{\text{eff}} \) at the initial stage could be attributed to low initial product temperature at the beginning of the drying process. The results also suggest that the influence of the initial period was very small compared to the total drying time and that \( D_{\text{eff}} \) can be fairly assumed to be independent from moisture concentration. The significance of considering the initial \( D_{\text{eff}} \) in the predictive ability of the model is discussed later.
Diffusion coefficient data for moisture transfer in plums during drying are not available in literature. However, the diffusion coefficient for similar products like grapes, apricots and apples may be found. Although it is difficult to directly draw comparison with these products it might further support the validity of the approach in estimating $D_{eff}$. Probably the most relevant data that could be used for comparison purposes are those from drying of grapes. Simal et al.\textsuperscript{79}, studying the drying of grapes obtained $D_{eff}$ values in the range $4.66 \times 10^{-10} - 1 \times 10^{-9}$ m$^2$/s at 80°C. Gekas\textsuperscript{143} reported apparent moisture diffusivities of around $2.55 \times 10^{-10} - 3.49 \times 10^{-10}$ m$^2$/s and $3.42 \times 10^{-10} - 4.9 \times 10^{-10}$ m$^2$/s for red grapes and white grapes, respectively during drying at 70°C. Diffusivity values for similar products are approximately consistent with the estimated $D_{eff}$ values for drying of plums.

### 3.3.4 Testing and Evaluation of the Diffusion Model

Figure 3.18 shows the comparison between the experimental and the predicted moisture content profile with time during drying at conditions of 80°C temperature, 5m/s velocity and 3% humidity. The predicted curves shown in this figure are those for the cases with and without incorporating the preheating period in the model. The initial preheating period was considered by using two values of $D_{eff}$ in the model, one that represented the initial period and the other for the rest of the drying process. Clearly, the model (with or without preheating period) predicted well the drying kinetics of plums under these conditions. In fact for plums dried from its initial moisture content down to about 20% moisture content (dry basis) the drying time was closely predicted. For instance, drying of plums down to 20% moisture content (dry basis) at these conditions took about 500 minutes whilst the predicted drying time from the model under the same drying conditions was about 502 minutes.

It can also be seen that better agreement exists between the experimental and predicted values when the initial preheating period is taken into consideration although the predicted drying times (at 20% moisture content) between considering the effect of preheating and not were the same. Ignoring the preheating process the model initially over-predicted the rate of drying. This is because the actual apparent diffusion coefficient is much lower at the early stages of the process compared to the overall $D_{eff}$. The $D_{eff}$ has a small value at the beginning of drying so that the rate of water loss does
appreciably alter in the subsequent stages. From the results, it was found that the initial effective diffusion coefficient ($D_{\text{eff}}$) at 80°C was about $4.28 \times 10^{-10}$ m$^2$/s whilst the $D_{\text{eff}}$ corresponding to the subsequent period was about $8.75 \times 10^{-10}$ m$^2$/s. It should be emphasised that the $D_{\text{eff}}$ at the preheating period has no physical meaning. This may only represent an empirical way of looking the different moisture movements during the initial heating period.

![Graph comparing experimental and predicted moisture content profiles](image)

**Figure 3.18.** Comparison between experimental and predicted moisture content profiles of plums during drying at 80°C (Rh=3%; V=5m/s; $MC_{\text{iwb}}=66\%$).

The above results indicate that the rate of internal moisture transport due to concentration gradients mainly controls the drying process under these conditions at 80°C. It should be noted that the prediction of the final drying time and the residual moisture content for a given set of conditions is of great importance for the stability of the product during storage and in evaluating the efficiency of the process. The results also show that heat transfer at the fruit surface during the initial stages of drying could be considered to improve the predictive accuracy of the model.
The diffusion model was further tested under moderate drying conditions to further ascertain the mechanism involved under these conditions. Experimental data conducted at drying conditions of 70°C, 5 m/s air velocity and 3% relative humidity were used. Results of the comparison between the predicted and the experimental values are shown in Figure 3.19. It is clear from the inspection of these curves that the numerical approach to simulate the drying behaviour of plums under these conditions may be less appropriate. The results indicate significant discrepancies between the predicted and experimental values. The experimental values were initially over-predicted by the model consequently causing systematic deviations between the predicted and experimental values throughout the entire drying process. From the results, plums dried down to 20% moisture content (dry basis) under these conditions would take about 910 minutes whilst the predicted drying time value was around 865 minutes.

Figure 3.19. Comparison between experimental and predicted moisture content profiles of plums during drying at 70°C (Rh=3%; V=5m/s; MC_{iwb}=66%).

Perhaps the discrepancy between the predicted curve and the experimental data particularly in the early stages of drying may be due to the preheating effect. Alternatively, as the results show that the plum has a greater initial resistance to
moisture transport than predicted, this may be a direct consequence of the effect of the skin layer. It should be noted that in this model the surface shell (skin layer) was assumed to reach equilibrium with the outside drying conditions instantaneously when evaporation commenced. This is because there is no resistance at the surface of plum and the rate of moisture flux was controlled by the rate at which the moisture diffuses from the interior to the surface. This may not be the case under these moderate conditions, and the skin plays an important role for at least part of the drying process.

This suggestion is consistent with the results of the previous chapter. It means that under these conditions at some stage particularly in the early part of drying the resistance to moisture movement is not probably distributed throughout the plum but was mainly concentrated at the surface shell (skin layer). The moisture loss process therefore depends mainly on the rate at which the moisture diffuses across the skin layer.

In view of the above, the effect of skin on the rate of moisture loss during drying was examined by drying plum samples without skin (chapter 2). Results of the experiments together with the predicted values are shown Figure 3.20. These experiments were conducted at drying conditions of 70°C, 3% humidity and an air velocity of 1 m/s. It was described previously that the rate of moisture reduction of plums without skin was faster compared to those with skin during drying at identical conditions. Also, the predicted result compares favourably with experimental data for plums dried without skin. In terms of drying time, the experimental drying of plums (without skin) down to 20% moisture content (dry basis) took 600 minutes whilst the predicted drying time was about 603 minutes. Coincidentally, the drying time (20% moisture content) of plums with skin was also closely predicted although the fitting was generally poor. In general, the experimental drying time for plums without skin was less than half that for plums with skin under the same drying conditions.

The result provides evidence of the importance of the skin layer to moisture transport at 70°C. This might indicate that the drying of plums with and without skin followed different drying mechanisms. This is evident from the close agreement between the predicted and experimental values for plums without skin and the poor agreement of the predicted and experimental data for plums having intact skin. During drying of plums
without skin the rate at which the moisture diffuses from the interior to the surface due to concentration gradients may be the predominating mechanism. Moisture reaching the surface is immediately in equilibrium with the drying air with no interfacial resistance.

Figure 3.20. Comparison between experimental and predicted drying kinetics of plums with and without skin (T=70°C; \(x\)=3\%; \(V\)=1m/s; \(MC_{\text{iwb}}\)=66\%).

On the other hand, it appears that during drying of plums having skin the resistance to moisture transfer is mainly exhibited at the skin layer. The relatively lower permeability of the skin layer under these conditions (as evident from lower moisture loss) may result in slowing down the movement of moisture internally. The results discussed in chapter 2 suggest a slower moisture movement across the skin layer compared to that within the flesh. In this case the \(D_{\text{eff}}\) in this shell may be less and consequently slows down the overall moisture loss. The current model assumed \(D_{\text{eff}}\) to be constant throughout the plum. Other authors have used a variable \(D_{\text{eff}}\) and assumed \(D_{\text{eff}}\) as a function of moisture content based on the nonlinearity of the plot \(\ln \text{MR}\) vs time of the drying curve.
In order to further explore these peculiarities, a plot of ln MR versus time for plums with and without skin was examined (Figure 3.21). Clearly, the figure shows a good linear fit for plums dried without skin, but a poor fit for plums dried with intact skin. This indicates that $D_{eff}$ within the flesh can be assumed to be constant. It also shows that $D_{eff}$ across the skin may vary with drying. This observation is consistent with the results discussed in chapter 2, which show that the permeability of the skin layer changes with drying time.

![Figure 3.21. Semi-log plots of the experimental moisture ratio (MR) versus time for plums dried with and without skin (T=70°C; ε=3%; V=1m/s; MC_{wb}=66%).](image)

The diffusion model enables the moisture distribution across the fruit to be established. The prediction of moisture profile is important in the determination of the extent of chemical reactions that occur during drying. Figure 3.22 shows the predicted moisture distribution as a function of both radial position and time during drying at 80°C. The plot illustrates the moisture content variation between locations from the stone-flesh interface to the skin layer. Curve 1 refers to the moisture profile at the stone-flesh interface and curve 2 for the subsequent radial position and so on until the last curve (curve 21) which represents the surface moisture profile. It can be seen that the
moisture content near the surface decreased rapidly with time. The moisture concentration gradients from the stone-flesh interface to the surface of the plum also decreased with the increase in drying time. The interior portions of the plum showed drying rates considerably less than portions near the surface. The figure also indicates that there are moisture concentration gradients inside the product at the end of drying. For plums dried down to an average moisture content of 20% (dry basis), the moisture content of the shell near the stone-flesh interface (curve 2) was about 50% (dry basis) whilst the moisture content of the shell near the surface (curve 20) was just around 3% (dry basis).

![Graph showing moisture content distribution within the plum during drying at 80°C (Rh=3%; V=5m/s; MC_{wb}=66%).](image)

**Figure 3.22.** Predicted moisture content distribution within the plum during drying at 80°C (Rh=3%; V=5m/s; MC_{wb}=66%).

This shows that the moisture contents at some points in the product were extremely very low. In turn, undesirable chemical reactions might take place in these portions of the product very quickly before equilibration was achieved. After drying, it is expected however that equilibration would normally take place rapidly. It should be noted that the availability of moisture distribution information within the fruit could further enhance a better understanding of chemical reactions taking place within the sample during drying.
process. This is because most of these reactions are dependent upon the water concentration. A typical example of the changes that accompanies dehydration of a food product particularly fruits is the non-enzymatic browning (i.e., Maillard and caramelisation). Aguilera et al. studied the extent of nonenzymatic browning that occurs during potato dehydration based on local and average moisture content. They found significant difference in the extent of nonenzymatic browning between using these values.

3.4 CONCLUSIONS

Two mathematical models were developed and tested against the experimental data to describe the drying kinetics of plums and to examine the mechanism of mass transfer involved. The proposed models were found to be applicable at different drying conditions. This may be evidence of different rate limiting steps being predominant under different conditions.

In plum drying, two major stages may be identified depending upon the external drying conditions. Initially a constant rate period of drying is often present where the rate of water evaporation from the fruit surface is the limiting factor to moisture loss. This is followed by a falling rate period where the rate of moisture loss is controlled by the rate of water diffusion through the fruit matrix. A mathematical model embracing these two concepts was found to work well at moderate drying conditions in particular at lower temperatures (60-70°C) where the external resistance is present and that the internal resistance is mainly characterised by a single falling-rate period. Results indicated that the approach of utilising the fruit temperature profile to estimate the associated parameters needed in the model was appropriate. However, at elevated temperatures (80°C and above) the two-regime model failed to adequately predict the moisture loss process. In this case, the moisture loss process might be expected to be predominantly controlled by the rate of internal movement driven by concentration gradient.

A numerical solution to the Fick's law of diffusion equation using finite difference method was adopted to describe the moisture transport during drying of plums at higher temperatures. In this model, the internal resistance to mass transfer was assumed to be uniformly distributed throughout the fruit. Independent determination of the effective
diffusion coefficient was found to be appropriate. The effective diffusion coefficient ($D_{eff}$) was observed to be independent of moisture content and the characteristic dimension of the plums. The estimated $D_{eff}$ varied with temperature according to an Arrhenius-type relation over the range of conditions considered. Incorporating the preheating period into the diffusion model improved its predictive potential although the estimated $D_{eff}$ during this early period has limited physical meaning.

The two proposed models provide useful information about the mechanism of mass transfer involved during drying of plums and could be applied for other similar foodstuffs.
Chapter 4

INFLUENCE OF CHEMICAL PRETREATMENT ON THE KINETICS OF DRYING PLUMS
4.1 INTRODUCTION

In the preceding chapters the rate of water transport across the waxy skin layer of the fruit has been shown to affect the drying kinetics of plums particularly at the early stages of the drying process. It was postulated that in the course of drying fruits having waxy skin surface, water loss may occur by means of different resistances to water transport. Water movement within the fruit matrix may be different from the rate at which the water diffuses through the skin layer. This is because the waxy skin layer has properties different from those underlying tissue. The most widely held view is that drying mechanism of these fruits may be mainly controlled by the resistance offered by the waxy skin layer for moisture transfer. It is known that the skin layer consists of a cuticle coated with waxes. Waxes deposited on the surface are believed to be hydrophobic in nature. The waxy skin layer, which represents an efficient barrier to water movement, has been the subject of numerous investigations. For instance, Martin and Stott demonstrated that the drying of grapes is only limited by the diffusion of water through the skin layer as peeled berries dried more faster than with skin intact. Water movement within the grapes was also reported to be faster compared with the water transfer through the skin. Similarly, studies have been conducted to investigate the role of the skin layer during drying. Weitz suggested that under solar drying conditions the resistance to water transports through the prune skin surface is the critical rate-controlling factor. Correspondingly, Chambers and Possingham concluded that hot air drying of grapes is a slow process owing to the resistance offered by the waxy outer skin of the fruit to moisture transfer.

It has been previously demonstrated that dipping treatments prior to drying could be employed to modify or remove the waxy cuticle. This is a chemical operation intended to disrupt the skin layer of the fruit thereby altering the water permeability. The process has also the tendency to remove the waxy bloom on the surface of the skin. This should accelerate the drying process as a result of an increase in skin permeability. The method of pretreatment evolved from the Greek procedure of dipping grapes in emulsions of olive oil and potash before drying. The drying emulsion used as pretreatment is usually made up of potassium carbonate and dipping oil in water.
Amounts of potassium carbonate and dipping oil vary depending on the application. In most studies with grapes\textsuperscript{44}, the drying emulsion usually contains 2.5% potassium carbonate and 2% drying oil. Optimum composition of the drying emulsion may depend on the types of fruit and the drying conditions employed. Drying oils mostly contain ethyl esters of fatty acids and emulsifiers.\textsuperscript{44} In order for the drying oil to be stable in water, an emulsifier must be added. Emulsifiers tend to reduce the interfacial tension between the two immiscible phases.\textsuperscript{166}

The mode of action of various dipping emulsions has also been extensively studied. Effect of drying emulsions can be separated into their components acting in an additive or possibly synergistic way.\textsuperscript{44} The dipping oil is considered the most important constituent in enhancing the drying process. Other components of the drying emulsion such as water, potassium carbonate, emulsifiers may have some additive influence. Ethyl esters of fatty acids were the most studied constituent of the drying oil. Grneravic\textsuperscript{167} observed that oleate esters exerted a marked effect on the rate of drying. Radler\textsuperscript{168},\textsuperscript{169} and others\textsuperscript{44},\textsuperscript{46},\textsuperscript{47} mentioned that ethyl esters of fatty acids i.e., ethyl oleate, ethyl stearate were the most effective. Fatty acid esters alter the crystallinity of the natural grape wax and thus lessen the resistance to water transfer.\textsuperscript{170} Other chemicals that are also found to be effective include NaOH.\textsuperscript{23},\textsuperscript{41} The use of an alkaline ethyl oleate as dipping treatment prior to drying of prunes has been reported to reduce the drying time substantially.\textsuperscript{46} The latest study of dipping on prunes was conducted by Barbanti et al\textsuperscript{22} who found that NaOH dipping reduces the drying time by about 30%. Similarly, recent studies\textsuperscript{44},\textsuperscript{171},\textsuperscript{172} have shown better results using a dipping emulsion (2% ethyl oleate in 2.5% aqueous potassium carbonate) in comparison to untreated grapes.

Commercial dipping oil such as "Voullaires EE-muls-oyle" is used in sultana production and contains 70-80% of a mixture of ethyl esters and emulsifiers.\textsuperscript{44} It is used as a component of the drying emulsion. The drying emulsion is composed approximately of about 1.5% commercial dipping oil and 2% potassium carbonate in water as recommended by the Commonwealth Scientific and Industrial Research Organisation (CSIRO).\textsuperscript{173} Recently, Uhlig\textsuperscript{44} showed that berries treated in 2.5%
aqueous potassium carbonate with 2% dipping oil lost weight about 3 times faster than the water-dipped berries.

In the prune industry, it was previously commercial practice in Australia and elsewhere to dip the fruit in a boiling caustic soda before drying. This procedure had the effect of producing very fine cracking or checking of the skin and sufficiently cut the bloom from the fruit surface leaving it thoroughly disorganized. However, the earlier use of aqueous caustic soda as a treatment for prunes prior to drying has ceased on the grounds that the extra cost of the process was not justified by the slightly increased drying rate.

It was therefore thought worthwhile investigating the use of drying oils, based on fatty acid esters, in the production of prunes. Its successful use in the sultana industry and elsewhere, together with prior work using pretreatments with drying prunes makes it attractive to try in an Australian context. This study was therefore conducted to evaluate the effect of various dipping pretreatments on the kinetics of drying plums. The focus was on exploring the applicability of a commercial dipping oil and looking its effect at different drying conditions to gain a better understanding of the rate-controlling mechanisms during drying. In addition, a number of ancillary techniques were used to assess the mode of action of the chemical pretreatments. The effect of pretreatment on the skin permeability was examined using a radiotracer technique. Then a pilot testing at the commercial level was carried out to investigate the feasibility of employing chemical pretreatment under the current prune drying practices and assessing the chemical residues left in the product. These aspects thus need to be elucidated before commercial adoption could be contemplated.

4.2 EFFECT OF FATTY ACID EMULSIONS ON THE DRYING KINETICS OF PLUMS

Based on earlier studies of using dipping emulsions to enhance the drying of waxy fruits particularly grapes, preliminary experiments were carried out to investigate the effect on the drying kinetics of the following pretreatments: 2.5% K$_2$CO$_3$ (aqueous) + 2% Ethyl oleate, 2.5% K$_2$CO$_3$ (aqueous) + 2% Ethyl stearate, distilled water + 2% Ethyl oleate, distilled water + 2% Ethyl stearate. Potassium carbonate was obtained from BDH
chemicals. Ethyl oleate and ethyl stearate were purchased from Aldrich chemicals. All the chemicals were of analytical reagent (AR) grade.

One litre of emulsion was prepared for each treatment. The pH of the mixture was determined using a Suntex SP-31 pH meter and was adjusted to pH 11 with 0.1M KOH or 0.1M HCl as necessary. The dipping emulsions were ultrasonicated (Unisonics) for 20 minutes to obtain a homogeneous mixture. Plum samples were dipped at room temperature except for ethyl stearate. Dipping of plum samples in ethyl stearate mixture was made at 40°C because of its melting point. Fresh plums were immersed into the dipping emulsion for 1 minute and gently agitated manually. After dipping, they were placed on a mesh tray at ambient conditions to evaporate the excess solvent from the fruit surface. This was done until the mass of the sample had reached to the same mass before dipping and then immediately loaded into the drying chamber. Pretreated plums were dried using the experimental setup described in Chapter 2. Drying experiments were carried out at drying air temperature and relative humidity of 70°C and 3%, respectively. In all cases the air velocity was maintained to about 1 m/s. Plum samples were also dried without pretreatment under the same drying conditions for comparison purposes. The drying procedure outlined in the previous chapter was employed in this experiment.

Figure 4.1 illustrates the effect of various chemical pretreatments on the drying kinetics of plums. As can be seen, all pretreatments increase the initial drying rates significantly and consequently reduce the drying time. Plums pretreated with an alkaline aqueous ethyl oleate mixture showed the highest drying rate followed by those pretreated with an alkaline ethyl stearate mixture. To reach 20% moisture content level (dry basis), untreated plums took 1190 minutes, 955 minutes for plums both pretreated with ethyl oleate alone and ethyl oleate in potassium carbonate and about 1110 minutes for plums pretreated with ethyl stearate alone and ethyl stearate in potassium carbonate. This is a reduction in drying time of almost 4 hours for plums pretreated with ethyl oleate and over 1 hour to those pretreated with ethyl stearate.
Figure 4.1. Effect of different dipping pretreatments on the rate of drying plums

(T=70°C; Rh=3%; V=1m/s; MC_{iwb}=69%).

The result shows that the rate of drying is dependent on the composition of the drying emulsion. The inferiority of ethyl stearate in increasing the drying rate could be partly due to the difficulty in forming a stable emulsion at approximately ambient conditions. Ethyl oleate was more convenient to handle and relatively easy to emulsify in cold water. Hence the use of ethyl stearate may not be desirable because of the difficulty associated with its melting point which would command an extra process.

Most previous studies have shown that dipping pretreatment enhanced the drying rate process. In particular, Masi and Riva\textsuperscript{146} studied the effect of pretreatment on the convective drying of grapes and observed that ethyl oleate modifies the water permeability of grape skin. Eissen et al\textsuperscript{171} obtained better results of solar drying grapes using 2\% ethyl oleate + 2.5\% K\textsubscript{2}CO\textsubscript{3}. Riva and Peri\textsuperscript{172} found a 25-33\% increase in drying rate of grapes pretreated with ethyl oleate alkaline (2\% EO + 2.5\% K\textsubscript{2}CO\textsubscript{3}) compared to the untreated. Ponting and McBean\textsuperscript{46} also studied the effect of different pretreatments on the kinetics of drying grapes, cherries and prunes and found that ethyl esters of fatty acids in the C\textsubscript{10}-C\textsubscript{18} range were the most effective compounds.
The application of drying emulsion may involve different possible modes of action. This could be either physical disruption or chemical change. Radler suggested that the fatty acids and their esters from a dipping mixture are absorbed and retained by the surface wax which establish a hydrophilic link between the hydrophobic surface of the grape and its watery contents, thus facilitating the flow of moisture through the cuticle. The hydrophilic groups on the wax surface are increased by reversible attachment of fatty acids and fatty acid esters. During drying, water diffuses through the skin tissue and enters the emulsion-filled capillaries of the wax layer in the liquid form. The dip emulsion then forms a continuous aqueous zone and allows water to reach the surface where evaporation normally takes place. In untreated sample, water has to vaporise in order to pass the waxy skin layer. This slows down the transport process of water.

The current result also shows the role of potassium carbonate in the dip. It was found that ethyl esters alone enhanced the drying process to a similar extent as in combination with potassium carbonate. This is in accordance with those observed by Uhlig who found that 2% ethyl oleate in water had an overriding effect on the mass loss of grape berries with no further mass loss could be induced by adding potassium carbonate. Ponting and McBean also reported that alkalis such as potassium carbonate had no value in reducing drying time when added to the dip. Similarly, Radler observed insignificant effect of adding potassium carbonate to the dip. Whilst Weitz et al indicated negligible advantage of potassium carbonate dip during solar drying of prunes. However, in some previous studies the inclusion of potassium carbonate in the dips was implicated to be necessary for saponifying the fatty acids as oleic, oleanoic and stearic present in the waxy skin layer. Accordingly, potassium carbonate appeared to influence the conversion of the wax from the hydrophobic condition, which is regarded as the important step and would probably facilitate the penetration of esters into the cuticle. Grncarevic demonstrated that grapes pretreated with potassium carbonate dried twice as fast as untreated. The dipping pretreatment may involve in attaching fatty acids and their esters to the wax surface possibly through potassium linkage. Probably, one of the important roles of potassium carbonate is to contribute to increase the pH, which assists in maintaining a stable emulsion of the oil in water.
carbonate does function to prevent the fermentation of oil and may assist in neutralising any free acids present in or on the skin.44

4.3 EFFECT OF COMMERCIAL DIPPING OIL ON THE DRYING KINETICS OF PLUMS

Commercial dipping oil known as "Voullaires EE-muls-oyle" is commonly used in sultana production as the oil component of the drying emulsion. A representative formulation of the drying emulsion of about 2% aqueous potassium carbonate with 2.5% of the commercial dipping oil was utilised. The amount of the dipping oil was increased from the recommended 1.5% (for grapes). This was compared with an experimental aqueous ethyl oleate dip (2% K₂CO₃+2.5% Ethyl oleate). Ethyl oleate was chosen to represent the oil component in the experimental dipping mixture because it is the active constituent in the commercial dipping oil. The commercial dipping oil was obtained from the Victorian Chemical Co. Pty. Ltd. The dipping procedure outlined in the previous section was employed in this experiment except that the dipping time was increased to 5 minutes (instead of 1 minute). The dipping time was raised in anticipation for commercial scale applications. The drying equipment and procedure described in the previous chapter were also utilised in this study. Drying experiments were carried out using an air temperature of 70°C, 3% humidity and 5 m/s velocity.

The result of the experiment is shown in Figure 4.2. Each drying run was carried out until the final moisture content reached 20% (dry basis). It was found that both pretreatments had a significant effect in reducing the total time of drying plums compared to the water-dipped pretreatment (control). The time required to dry the untreated plums down to the above moisture level was about 910 minutes whilst drying of plums pretreated with ethyl oleate solution took 775 minutes and 840 minutes for plums pretreated with commercial drying emulsion. This means a reduction in drying time of about 2 hours for plums pretreated with ethyl oleate dip and over one hour for plums pretreated with commercial drying emulsion. Thus the commercial drying emulsion is not as effective as the experimental ethyl oleate dip.
The reason for the observed effect of dipping pretreatments could be due mainly to the modification or disruption of the waxy skin layer which presents a discontinuity of moisture flow between the aqueous interior of the fruit and the drying air. It is also likely that dipping pretreatment may have modified the hydrophobic nature of the waxy layer thus facilitating efficient flow of moisture. Uhlig\textsuperscript{44} suggested that the added hydrophilic groups from the drying oil impart the properties necessary for the transport of water molecules and that the adsorption of fatty acid esters of the drying emulsion would establish a hydrophilic link between the hydrophobic surface of the fruit to the aqueous interior. Van Overbeek\textsuperscript{177} explained that during drying the water content of the cuticle and underlying tissues decreases, thus pulling the surface wax units closer together. The presence of dipping emulsion applied might prevent or at least hinder this process.

The documented variation in the effectiveness between the two pretreatments could be attributed to the difference in the concentration of ethyl oleate in the dips. Ethyl oleate component in the commercial drying emulsion is much lower than that in the
experimental ethyl oleate dips (about 30% less). According to Ponting and McBean\textsuperscript{46}, the rates of drying increase with increasing ethyl oleate concentration. They found out that the optimum concentration of ethyl oleate in the dip appears to be about 2-4\% for prunes. It should be noted that the commercial dipping oil was formulated specifically for grapes.

Because of the natural variation between types of fruit and the difference in the conditions employed during drying the effect of a specific pretreatment may vary considerably. A significant difference into the effect of dipping pretreatments on plums obtained from different picking seasons was observed. The results show that utilizing plums obtained from 1996 picking season (Figure 4.1) the ethyl oleate pretreatment for instance was more effective than those plums from 1997 season (Figure 4.2). It indicates an almost 4 hours reduction in drying time of plums from the 1996 season and just about 2 hours from the 1997 season although the later was pretreated with much higher ethyl oleate concentration. This finding could be attributed to the variation of fruit between seasons particularly the amount of waxes deposited on the surface layer of the skin and the drying conditions. It was noted that during the 1997 season the plums matured under near-drought conditions. According to McBean et al\textsuperscript{178} these environmental conditions would result to developing a relatively heavy layer of waxes on the skin surface. The result might have also affected by the degree of maturity at harvest. Using an electron microscopy, Bain and McBean\textsuperscript{8} showed that the generation of wax layer in the skin increased with maturity.

Since dipping pretreatments resulted in significantly varying the drying rates it can be concluded that under the drying conditions studied the evaporation of water from the fruit surface to the drying air is not the rate-controlling mechanism. A significant variation in the drying characteristics particularly at the early stages of drying clearly leads to suggest that the movement of moisture across the skin layer is an important mechanism. This behaviour was examined further by plotting of drying rate versus moisture content for the above data. The result is notable in that it is difficult to see the constant period (Figure 4.3). This confirms that the drying process under these conditions is not evaporation rate-controlled mechanism. If the drying process is then governed by the movement of moisture within the flesh, then pretreatment would
probably have no such influence the fact that it is mainly affecting the waxy skin layer as previously demonstrated from several works. However, because of a significant difference in drying rate as observed particularly at the early stages of drying suggests that the skin layer is involved in the mechanism. From the figure, the drying curves for untreated and pretreated plums start to converge at moisture content of about 0.8-0.9 kg moisture/kg dry matter. The convergence may signify the start of internal diffusion rate-controlling mechanism. It is known that during this period the moisture concentration gradient across the fruit is the main driving force for mass transfer assuming insignificant temperature gradient within the fruit. This implies that at the early stages of drying where there is considerable difference in the drying rate the moisture movement is mainly restricted at the skin layer.

![Figure 4.3](image)

**Figure 4.3.** Effect of different dipping pretreatments on the rate of drying plums 
(T=70°C; Rh=3%; V=5m/s; MC\textsubscript{iwb}=66%).

Clearly, the results indicate that the role of pretreatment is likely to be significant at the stage where the rate of water transport across the skin is surpassed by the rate of water diffusion within the fruit matrix. Thus the decisive effect of pretreatment is only obvious at the early stages of drying and that the dipping pretreatment does not have a significant
influence on the drying process once its mechanism is controlled by the movement of moisture within the fruit matrix. Correspondingly, Suarez\textsuperscript{179} showed that the effectiveness of ethyl oleate is less significant at lower moisture content. From the above results, it is likely that the magnitude of the effect of a drying emulsion is a function of drying conditions. It is therefore interesting to investigate the effectiveness of pretreatment at various drying conditions.

4.4 EFFECT OF CHEMICAL PRETREATMENT AT DIFFERENT DRYING CONDITIONS

In spite of the reduced effectiveness of the commercial drying oil in comparison to the ethyl oleate, its performance was further examined at different drying conditions. This was necessary to maximise its effect because of the greater potential application in the prune industry due to its availability and costs. Table 4.1 summarises the results for the experiments on the effect of dipping pretreatment at different drying conditions. The values in the table are the average of at least two experiments.

Table 4.1. Effect of dipping pretreatment (2\% K$_2$CO$_3$ + 2.5\% Voullaires oil) under different drying conditions on the total drying time (Final MC = 20 \% dry basis).

<table>
<thead>
<tr>
<th>Drying conditions</th>
<th>Drying time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>untreated</td>
</tr>
<tr>
<td>1. Effect of air temperature [V = 5 m/s; Rh = 3%]</td>
<td></td>
</tr>
<tr>
<td>70°C</td>
<td>910</td>
</tr>
<tr>
<td>75°C</td>
<td>720</td>
</tr>
<tr>
<td>80°C</td>
<td>500</td>
</tr>
<tr>
<td>2. Effect of air velocity [T = 70°C; Rh = 3%]</td>
<td></td>
</tr>
<tr>
<td>1 m/s</td>
<td>1210</td>
</tr>
<tr>
<td>5 m/s</td>
<td>910</td>
</tr>
<tr>
<td>3. Effect of air relative humidity [T = 70°C; V = 1 m/s]</td>
<td></td>
</tr>
<tr>
<td>3 %</td>
<td>1210</td>
</tr>
<tr>
<td>31 %</td>
<td>1275</td>
</tr>
</tbody>
</table>
In this study, the commercial "Voullaires EE-muls-oyle" was used as a representative dipping oil component in the drying emulsion for all tests. A drying emulsion containing $2\% \text{K}_2\text{CO}_3 + 2.5\%$ Voullaires oil was also used as a standard mixture. The dipping procedure outlined in the previous section was used in this experiment. The influence of the commercial dipping emulsion was investigated under different drying air temperatures (70, 75 & 80°C). Its effect was examined at two levels of relative humidity of the drying air (3% and 30%). The effect of pretreatment at different air velocities was examined at 1 and 5 m/s. Pretreated and untreated plums were dried using the experimental setup and procedure described in Chapter 2.

### 4.4.1 Drying Air Temperature

The data in the table present the effect of dipping pretreatment on the drying kinetics of plums at different drying temperatures. It is apparent from the results that increasing the drying air temperature, the effect of dipping emulsion becomes less important. The obvious effect of dipping pretreatment is only manifested at the lowest drying air temperature (70°C) studied. Drying of pretreated plums down to a final moisture content of 20% (dry basis) at 70°C would take about 70 minutes less than those untreated plums. Whilst at 80°C temperature, both untreated and pretreated plums were dried to the same time.

These results are in accordance with the previous results and mechanistic studies in chapters 2 and 3. It was concluded there that at moderate temperatures, skin resistance is important to the rate of drying. Consequently the effects of pretreatment, directed at disrupting the skin layer and increasing the permeability to water are likely to be manifest under these conditions. At higher temperatures the skin plays a minor role, the rate-determining step having been shown to be mass transfer through the flesh of the fruit.

Ponting and McBean\(^46\) showed that at higher drying temperatures the drying time for prunes was influenced more by temperature than dipping pretreatment pointing out that the vapor pressure inside the fruit increases with increased temperature so that the restricted effect of the skin to passage of water vapor becomes negligible. These authors
concluded that chemical pretreatments hasten the drying rate during the early period of drying grapes and other waxy fruits. The length of the skin rate-limited period is probably dependent upon the properties of the waxy skin layer, which in turn a function of drying temperature. The longer this period in a particular drying process the greater the effect of dipping pretreatment. Obviously, at elevated temperatures this period is less significant than at a lower temperature because of the faster initial drying rate.

The increased drying rate at higher temperature could be attributed to the greater drying potential of the air and the significant changes to the structure of the skin brought by intense heating. Martin and Stott\textsuperscript{96} mentioned that the permeability of the cuticle increases with temperature and that water movement through the parenchymal cells is faster compared with that through the skin. Unpublished data of Johnson and McBean as cited by Bain and McBean\textsuperscript{7} suggested that the lowest melting point of any component of prune wax is 56°C, while the wax, as a whole does not melt until about 65°C. Bain and McBean\textsuperscript{8} investigated the changes in structure of the waxy layer in plums brought about by increasing temperature (49°C to 63°C) during drying using carbon replica of electron microscopy. They found that the normal surface structure showed some alterations at 54°C, but was not completely disorganised until 66°C. In recent study\textsuperscript{119}, it was demonstrated by SEM analysis that the plum surface structure was significantly disrupted during drying at 80°C. This would have significantly left the skin’s water-barrier properties inefficient.

4.4.2 Drying Air Velocity

It is evident from the analysis of the data in Table 4.1 that the drying rate of pretreated plums is much faster than that of untreated plums at higher air velocity. The effect of pretreatment at lower air velocity is less. At higher air velocity, the drying time required to reach 20% moisture content (dry basis) for pretreated plums was about 70 minutes shorter compared to those untreated plums. Whilst at lower air velocity the difference in drying time between pretreated and untreated was just around 40 minutes.

The result indicates that the dipping pretreatment process is more effective at higher air velocity. This is in agreement with Barbanti et al\textsuperscript{22} who stated that a combination of
high air velocity (4 m/s) and NaOH dipping pretreatment gave the shortest time during drying of Stanley plums. The trend may be assigned to the rate-controlling mechanism predominant at a certain condition. Probably at lower air velocity the moisture loss process is limited by the maximum evaporation potential. At higher air velocity, the rate of moisture loss may be controlled by the rate of water diffusion across the skin layer. Hence modifying the skin permeability through pretreatment further enhanced the drying process. Usually the air velocity is of great importance during the period where there is rapid movement of abundant moisture to the fruit surface. During this period a higher air velocity may be necessary to remove the available moisture. Also, an increase in air velocity probably triggers the greater rate of moisture movement across the skin due to increase in heat transfer between the air and fruit. At higher air velocity, the moisture in the surface is removed at faster rate. Such action may create a considerable gradient potential driving the moisture across the skin layer to a greater extent and therefore further aided the effect of pretreatment. According to the results, high air velocity seems to maximize the effect of dipping pretreatments.

4.4.3 Drying Air Relative Humidity

The influence of dipping pretreatment on the drying of plums at different air relative humidities was investigated. Comparison of the drying time between untreated and pretreated plums during drying at different air humidity is also shown in Table 4.1. Drying experiments were carried out at drying air temperature and velocity of 70°C and 1 m/s, respectively. The result shows that there is very little difference between untreated and pretreated plums during drying at higher air humidity. At lower air humidity, the drying process of pretreated plums is much faster than the untreated plums. The plums were dried until their moisture content reached to 20% (dry basis). It was observed that the difference in drying time between untreated and pretreated plums at lower air humidity was about 40 minutes whilst at higher humidity the untreated and pretreated plums were dried at the same time.

The result indicates that pretreatment does not appreciably influence the drying kinetics at higher air humidity. Obviously, the potential of the drying air to absorb moisture from the material is greatly reduced at higher humidity. Thus under this condition the rate of
moisture loss may be limited by the maximum evaporation potential of the drying air. Hence further increase in the skin permeability through pretreatment does not alter the drying rate. As expected, the presence of relatively higher moisture in the drying air inhibits a lower concentration gradient between the drying air and the fruit. This reduces the driving force for mass transfer, which probably affects the rate of movement of moisture across the skin. As the moisture content of the drying air increases, its suppressing action is markedly increased creating a lower rate of moisture movement across the skin. At higher air humidity the expected increase of drying rate due to increase skin permeability brought by pretreatment is probably compensated with lower driving force for moisture transfer. This may result in a negligible difference in drying rate as observed between untreated and pretreated samples under this condition. The result implies that the moisture concentration of the drying air may also affect the rate of moisture transport across the skin. On the other hand, decreasing the moisture content of the air, increases its ability for drying. This might result in the situation in which the rate of moisture loss is controlled by the water movement across the skin layer. Thus lower humidity of the drying air seems to be more conducive to a dipping pretreatment process.

4.5 EFFECT OF DIPPING PRETREATMENT ON THE FRUIT SKIN PERMEABILITY

To explore further the effect of pretreatment on the drying behaviour it was necessary to look at the skin permeability of plums. Water permeability of the plum skin as affected by dipping pretreatment process was examined using a radiotracer method. Fresh plums were pretreated with 2% K$_2$CO$_3$ + 2.5% Voullaires oil drying emulsion. The dipping procedure outlined in the previous section was employed in pretreating the fresh plums. The apparatus and procedure for the radiotracer technique described in chapter 2 were utilised in this experiment.

Results of the experiments are illustrated in Figure 4.4. The experimental data were the average of at least three runs. It appears from the figure that the skin permeability of untreated plums is greater than the pretreated plums. The difference is only slightly larger than the combined experimental error and there may be no real difference in skin
permeability between untreated and pretreated fresh plums and that the slight variation could be due to some artifacts. This could be mainly due to the natural variation of the skin layer between individual fruit. Inconsistency in the extraction of representative skin sample from the fruit may have also contributed to this effect. In this experiment, the plum samples were washed with water during the extraction of the skin. The extraction of the skin was done about 30 minutes after dipping. Several researchers have indicated that washing may reverse the effect of pretreatment. Dudman\textsuperscript{45} and Grcarevic\textsuperscript{167} have shown that dipping pretreatment does not permanently alter the rate of water loss so long as the treated grapes are washed within 24 hours of drying. They further mentioned that the effects of dipping emulsion are essentially reversible and that little wax is removed by dipping. These workers showed that when grapes were washed within 24 hours the effect of dipping was reversed. Van Arsdel et al\textsuperscript{180} also pointed out that washing reverses the effect of treatment.

**Figure 4.4.** Effect of dipping pretreatment (2.5% K\textsubscript{2}CO\textsubscript{3} + 2.5% Voullaires oil) on plum skin permeability using radiotracer method.
4.6 EFFECT OF PRETREATMENT ON THE RATE OF WATER LOSS DURING AMBIENT STORAGE

The rate of mass loss at ambient storage conditions for partially dried plums was studied to generate more facts of the effect of pretreatment on the drying kinetics of plums. A dipping emulsion containing 2% $\text{K}_2\text{CO}_3 + 2.5\%$ Voullaires oil was used as a pretreatment in this experiment. The details of the experimental procedure are presented in chapter 2.

The untreated and pretreated plums partially dried to different times and temperatures were allowed to dry further at ambient storage conditions. The rate of mass loss during ambient storage was monitored and plotted against time. This condition was selected because it has been established that the dipping pretreatment may be more effective at milder temperature. The mass loss profiles during ambient storage of untreated and pretreated plums partially dried to 2 hours and 4 hours at 70°C are shown in Figure 4.5.

![Graph showing mass loss vs. time for untreated and pretreated plums](attachment:image.png)

**Figure 4.5.** Effect of pretreatment ($2\% \text{K}_2\text{CO}_3 + 2.5\%$ Voullaires oil) on the rate of mass loss during ambient storage of partially dried plums ($T=70°C; \text{Rh}=3\%; V=5\text{m/s}; \text{MC}_{\text{wb}}=66\%$).
It was found that the moisture contents of the untreated and pretreated plums after 2 hours of drying at 70°C were about 1.50 (kg H₂O/kg dry matter) and 1.47 (kg H₂O/kg dry matter), respectively. Whilst after 4 hours of drying, the moisture contents for untreated plums were 1.09 (kg H₂O/kg dry matter) and 1.00 (kg H₂O/kg dry matter) for pretreated. The effect of dipping pretreatment on the rate of mass loss during storage is obvious for plums dried at this temperature. From the figure, the mass loss rates of untreated and pretreated partially dried to 4 hours were initially higher than those dried for 2 hours while both maintaining considerable differences between untreated and pretreated.

The results suggest that plums partially dried to various times may have experienced different degree of damage to the waxy layer. It may be also suggested that the dipping pretreatment imparted significant change in the effective skin permeability. Uhlig demonstrated that there were structural collapse and loss of complex arrangement of the overlapping wax platelets of grapes through the emulsion treatment of 2.5% K₂CO₃ + 2% Voullaires oil. SEM replicas of plum fruit taken after dipping in near boiling 0.2% sodium hydroxide showed structural loss. However, Chambers and Possingham found that the dipping of sultanas in alkaline emulsions increased the rate of sun drying without altering the natural structure of their skin layer. They theorized that the result could be mainly due to the conversion of the hydrophobic wax layer into hydrophilic by flooding the small spaces in the wax layer with emulsions thus facilitating the ease of water movement. Because of the difference in the rate of moisture loss between untreated and pretreated plums during ambient storage, it may be possible that the moisture loss is not limited by the rates of water movement within the flesh and the evaporation from the fruit surface. This means that the moisture loss process is mainly controlled by the rate of diffusion across the skin layer. This phenomenon was ascertained by the fact that the plums which were dried to 4 hours exhibited a higher mass loss rate although they were dried to much lower moisture content than those dried for 2 hours. However, the final period of drying particularly for plums dried to 4 hours may be characterised by diffusion controlled mechanism within the flesh as the curve started to diverge.
The rate-controlling diffusion within the flesh is further demonstrated in Figure 4.6 where drying was carried out at a high temperature. The moisture contents of the untreated and pretreated plums were reduced both to 1.18 (kg H₂O/kg dry matter) after 2 hours of drying. After 4 hours of drying, the moisture contents of the untreated and pretreated plums were found to be 0.71 (kg H₂O/kg dry matter) and 0.68 (kg H₂O/kg dry matter), respectively. Both untreated and pretreated plums dried for 6 hours resulted to moisture contents of about 0.41 (kg H₂O/kg dry matter) and 0.38 (kg H₂O/kg dry matter).

![Figure 4.6](image)

**Figure 4.6.** Effect of pretreatment (2% K₂CO₃ + 2.5% Voullaires oil) on the rate of mass loss during ambient storage of partially dried plums (T=80°C; Rh=3%; V=5m/s; MCᵢwb=66%).

It was noticed in this figure that the effect of pretreatment is not visible. This result is consistent in what has been previously observed. Clearly, the dipping pretreatment is not effective at the stage where diffusion within the flesh dominates the process. From the figure, it may be possible that the rate of water diffusion within the fruit matrix is the main governing process during the storage of plums dried for 6 hours. The plums dried for 2 and 4 hours showed initial convergence and much higher rates than the plums
dried for 6 hours. The initial convergence may signify the period in which there is free moisture within the flesh for fruit dried for 4 hours until it deviates from the trend. For plums dried to 2 hours, this period may be much longer. Although there appears considerable free moisture within the fruit matrix after 2 hours of drying but because the dipping pretreatment is not effective suggests that the restrictive effect of the waxy layer to the passage of moisture becomes insignificant. The above results further indicate the importance of the waxy layer of the skin during drying process of plums.

4.7 COMMERCIAL SCALE TESTING OF DIPPING PRETREATMENT

METHOD

Because the dipping pretreatment offered promising advantages under simulated laboratory drying conditions, further tests were conducted on a commercial scale. The commercial "Voullaires EE-muls-oyle" was used as a representative dipping oil in the drying emulsion because of its greater potential application to the prune industry due to its availability and cost in comparison to ethyl oleate. The trial was carried out at Kingsvale, New South Wales, Australia. In Australia, it is normal commercial practice to wash the fruit in cold water before they are dried to remove the orchard dusts and other dirt. This makes it easy to incorporate any pretreatment into the current system. Fruit samples were dipped into a water bath of 1200 L aqueous mixture containing about 2.5% K₂CO₃ + 1.5% Voullaires' oil. The dipping mixture was fully agitated before dipping the plum samples. Unloading of the pretreated fruit from the water bath was made through a conveyor belt. This arrangement allowed the fruit to be exposed to the dipping emulsion for about 5-20 minutes. They were conveyed directly to a mechanical grading system. Graded fruit were manually loaded onto the trays. The plums are spread in a single layer and the trays are stacked onto trolleys. The control samples were normally dipped in cold water.

During the trial, each tunnel dehydrator of parallel-flow type was only operated with six trolleys of fruit. One dehydrator was used for drying the pretreated plums while the other dehydrator was utilized for drying the untreated plums to serve as control. The trolleys were loaded one at time in one end of the dehydrator tunnel. Loading of pretreated and untreated fruit into the drying tunnel was performed simultaneously at 2
hours interval. Three trolleys of fruit for each treatment were used in this trial. During loading, trolley at inlet end of the tunnel was turned around to ensure uniform drying and the trolley at the outlet side of the tunnel was checked for dryness and unloaded if necessary. Usually, checking the dryness of the fruit at the outlet end of the tunnel is simultaneously performed during loading/unloading period to minimise heat losses due to frequent opening of the doors. The dryness of the fruit was determined by visual inspection employing the operator's skills and experience based on the "toughness" of the dried prunes by gentle squeezing. After drying, about 5 kg of dried prune samples were taken drawn from 5 different locations on each sample trolley to ensure a representative sample. These samples were used for final moisture content determination and other chemical analysis.

Table 4.2. Final moisture content (% dry basis) of untreated and pretreated plums dried in parallel-flow commercial prune dehydrator.

<table>
<thead>
<tr>
<th>Location</th>
<th>Moisture content (% dry basis)</th>
<th>Untreated</th>
<th>pretreated</th>
</tr>
</thead>
<tbody>
<tr>
<td>top centre</td>
<td>29.00</td>
<td>26.50</td>
<td></td>
</tr>
<tr>
<td>mid left</td>
<td>23.70</td>
<td>19.40</td>
<td></td>
</tr>
<tr>
<td>mid centre</td>
<td>28.10</td>
<td>21.70</td>
<td></td>
</tr>
<tr>
<td>mid right</td>
<td>26.10</td>
<td>23.20</td>
<td></td>
</tr>
<tr>
<td>bottom centre</td>
<td>26.30</td>
<td>20.20</td>
<td></td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>26.64</strong></td>
<td><strong>22.20</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Standard deviation</strong></td>
<td>2.05</td>
<td>2.81</td>
<td></td>
</tr>
</tbody>
</table>

Results of the commercial scale trial initially showed no clear advantage in employing the dipping pretreatment process. Both untreated and pretreated plums were removed from the dehydrator after 12 hours. It should be borne in mind that the determination of the final moisture content was solely based from the operator's discretion and experience. In practice the dryness of the plums is checked every 2 hours to avoid excessive heat losses due to frequent opening of the doors. However, it was possible to re-assess the moisture content of dried prunes in the laboratory. This analysis would
provide more credible facts of the effect of pretreatment under the commercial scale. The results of the analysis are presented in Table 4.2. Data shown in the table indicated that the untreated plums were slightly dried to higher final moisture content than the pretreated plums. The pretreated plums had final moisture content of about 22.2% (dry basis) whilst the untreated plums had 26.6%: a difference of about 4.4% moisture content.

In the parallel-flow method of drying, the fruit experience severe heating at the early stages of drying. As the drying progresses, the fruit were subsequently exposed to gradually decreasing temperature along the length of the tunnel. Given the inlet temperature of about 82°C, the fruit surface could rise to more than 65°C soon after their entry into the tunnel as demonstrated in laboratory experiments. This would significantly modify or disrupt the waxy skin layer resulting in losing its ability to restrict water movement. It should be noted that pretreatment is most effective at the early stages of drying where there is considerably high concentration of free moisture within the fruit and that the rate of water loss is predominantly limited by the skin layer. Under the parallel-flow drying conditions this period may relatively short. The observed insignificant difference in drying time between untreated and pretreated confirms what has been established in laboratory experiments. McBean et al\textsuperscript{41} also showed that under parallel-flow conditions of drying, untreated plums dried at the same rate as plums which had been de-waxed by a light petroleum treatment. However, there is some evidence that the pretreatment process does have some effect as shown from the observed difference in the final moisture content of the dried prunes. This is because the plums were subjected to reducing temperature in the subsequent stages of drying.

The results generally suggest that under parallel-flow conditions of the current commercial prune drying the waxy layer does not hinder water transport through the skin. It is likely that the effect of dipping pretreatment would be of great significance in the conventional counter-flow drying in which fruit enter the cold end (about 55-60°C) of the drying tunnel and progresses in opposite direction with the drying air toward the hotter end (about 75°C).
A preliminary chemical analysis was carried out to investigate the amount of residues left on the dried prunes due to pretreatment. This was done immediately after the trial using a gas chromatography-mass spectrometry (GC-MS) technique to identify and quantify the pretreatment residues. A mixture containing 0.76mg of drying emulsion per 1mL of isooctane was prepared as a standard. Extraction of the residues was carried out by dipping dried prune samples into a 5mL of isooctane and then ultrasonicated for about 5 minutes. About 10μL of the solution was taken and injected into the GC-MS. Results of the analysis indicate that only the ethyl oleate constituent could be detected in pretreated dried product. It should be noted that this compound is the main component of the dipping emulsion. The concentration of ethyl oleate was found to be about 5mg per kilogram of dried prunes.

Dried prunes are usually rehydrated to obtain a final product that is ready for consumption. Problems associated with the presence of chemical residues in the final product were further assessed. The possibility of disintegration of prunes during rehydration was also examined. The reason for this is that it was found previously that pretreatment with alkaline caustic soda resulted in poor fruit integrity on rehydration. After 4 months of storage the pretreated dried prunes (from the trial) were then commercially rehydrated to assess these problems. During rehydration, the dried prunes were washed with cold water prior to cooking with steam. Prunes were then exposed for about 45 minutes inside the cooking oven heated with a steam of about 90°C temperature before conveyed to the packaging system to obtain the final product. Analysis of water from the washing tank was also carried out. This was done by taking water samples after rehydration process in each section. Quantification of the chemical residues was done using a gas chromatography (GC) technique. Extraction of the residues from the final product was carried out using similar procedure as described above. Residues from water samples were examined by adding with isooctane. The solution was then mixed thoroughly for about 1 hour. Water was allowed to settle and the isooctane portion was carefully extracted. About 10μL was taken from the extracted solution and injected into the GC system. A standard run of known ethyl oleate concentration was also carried out.
Results of the analysis showed that the residues in dried prunes were further removed during the rehydration process. This is because the constituents of the drying emulsion may have only penetrated at the skin layer. Uhlig\textsuperscript{44} showed that the dipping components penetrated no further than the cuticular layer of a grape. The amount of ethyl oleate in water from the cooking oven was found to be about 2.4 mg per kg of dried prunes. No traces of ethyl oleate could be detected in water from the washing tank. The amount of residues left in the final product was also found to be about 1.53 mg per kg of rehydrated product (which correspond to 1.78 mg per kg of dried prunes). These findings suggest that there would be no problem of incorporating the pretreatment from the production and rehydration side. In addition, the drying oil used commercially is of food grade.

4.8 CONCLUSIONS

The present study was conducted in order to explore the possibility of using dipping pretreatments to enhance the drying process of prunes. Effects of various pretreatment emulsions were investigated. The effectiveness of the dipping pretreatments at different drying conditions was also examined.

Results of the study indicate a significant effect of dipping emulsions on the kinetics of drying plums particularly at the early stages. Ethyl oleate dip was found to exhibit greater effect on the average drying rate. It was also observed that the addition of potassium carbonate to the dips did not alter the drying behaviour. The commercial drying emulsion commonly used for grapes was applied to prunes and found to be less effective compared to the ethyl oleate dip. At elevated temperatures the commercial drying emulsion was ineffective. It was further observed that the effect of the drying emulsion was greater at higher air velocity. The use of lower relative humidity of the drying air was found to be more conducive for the dipping pretreatment to hasten the drying process. The SEM work of Uhlig\textsuperscript{44} on grapes, which showed significant difference in the structural loss of the wax layer between untreated and pretreated, further confirmed the effect of pretreatment.
The results with the pretreatment of fruit at different conditions confirmed earlier idea in chapter 2 and 3 about the mechanisms of moisture loss. In particular the ineffectiveness of pretreatment at higher temperatures was in keeping with the predominance of internal moisture transfer under such conditions.

The effect of the dipping pretreatment was examined at a commercial level. It was found that the dipping pretreatment was less effective at the current parallel-flow method of drying prunes. This is due to the fact that this method of drying employs initially higher temperature causing the waxy skin layer of the fruit to lose its water-barrier properties at early stages of drying. The counter-flow configuration of drying prunes would probably reap the benefit of the pretreatment procedure because this method of drying uses initially much lower temperature such that the water restriction at the waxy layer is expected to be significant. Washing the fruit prior to drying provided a relatively easy way to incorporate the dipping pretreatment procedure into the current practice. The commercial-scale testing results further confirmed the dependence of the effectiveness of dipping pretreatment on the drying conditions. It also showed that any problems of disintegration during rehydration are unlikely and that there was very little problem of chemical contamination either in the product or in the processing equipment.
Chapter 5

THE KINETICS OF CARBOHYDRATE CHANGE DURING DRYING OF PLUMS
5.1 INTRODUCTION

It has been mentioned in previous chapters particularly in chapter 2 that mass losses other than the evaporation of moisture are occurring during the drying of plums. The observed mass losses in excess of the initial moisture content, particularly at elevated temperatures were a clear indication of this phenomenon. This suggests that other, chemical, changes of the components present in plums are taking place during drying. Monitoring the chemical compositions of plums and any changes during drying has important implications for the final quality of the product.

Carbohydrates are significant components found in most plum cultivars. Plums are known to contain the four major simple carbohydrates such as glucose, fructose, sucrose and sorbitol. The carbohydrate composition of the plums was reported to vary with cultivar. Forni et al.\textsuperscript{9} examined the carbohydrate content of 13 different cultivars but none of these were d'Agen variety. Preliminary studies from this laboratory by Newman\textsuperscript{15} and Wilford\textsuperscript{14} were the only available information on the carbohydrate content of d'Agen plums.

Newman\textsuperscript{15} and Wilford\textsuperscript{14} followed the carbohydrate content profile as a function of drying time. Their work has been limited to investigating the effect of temperature and other drying conditions such as relative humidity and velocity were not either monitored or studied. Other than these, there has been little work on the kinetics of carbohydrate changes during drying of plums as influenced by different drying conditions. On the other hand, the pH of plums has been reported by numerous authors to vary between cultivars. It is known that the sugar degradation reactions are pH sensitive. At present, no specific study has been found in the literature, which investigates the influence of fruit pH on the kinetics of carbohydrate changes during drying. The determination of pH and its effect on sugar degradation reactions during drying may provide valuable information on the likely mechanism dominating during drying process. It should be noted that dried prunes are usually stored often for up to 1 year before subsequent processing. It is therefore of great interest to determine any further chemical reactions occurring during storage. This may have significant impact on the storage stability of the dried product and on the final organoleptic qualities of prunes.
Better understanding of the chemical changes occurring during drying and storage would therefore be useful in devising an efficient drying system which could be employed to obtain a high quality dried product. This is important in identifying the onset and rate of chemical degradation reactions occurring during drying. It has also major implications for the control of product quality and selection of the final conditions of the dried product. In fact, knowledge of the chemistry of drying plums may provide valuable information in the development of physical drying models and would further increase our understanding of the drying mechanism as the sugar concentrations may affect the diffusion process of moisture within the fruit matrix. The work of Marousis et al\textsuperscript{162} on the effect of sugar on the mobility of water in amioaca starch during air drying at 60°C is a typical example which showed a significant decrease in water diffusivity as the sucrose concentration was increased from 5 to 25% (dry basis).

This chapter covers extensive studies of the carbohydrate contents of the plums and their changes during drying. The influence of the different conditions of the drying air such as temperature, relative humidity and velocity on the kinetics of carbohydrate change was studied in detail. The effect of pH of the fruit on the carbohydrate degradation reactions during drying was also investigated. In addition, the carbohydrate content of the dried product was monitored during prolonged ambient storage. Chemical compositions of prunes commercially dried using different methods of drying together with their changes during storage were analysed.

### 5.2 MATERIALS AND METHODS

#### 5.2.1 Preparation of Dried Fruit Samples

The analyses of carbohydrates were conducted on plums taken from the batch of samples collected during 1996 and 1997 picking seasons. Plums were dried using the experimental drying setup and procedure described in chapter 2. Three major conditions of the drying air were studied; temperature, relative humidity and velocity. The effect of drying temperatures in the range of 70-90°C was investigated. Two levels of relative humidity (3% and 30%) and two air velocities (1 and 5 m/s) were also studied. These conditions were selected to simulate the drying conditions used commercially. The
individual weights of plums were recorded before being arranged on the tray. A batch of six plums was removed at regular intervals (about 1 hour) during drying. Each batch was composed of plums randomly selected in different locations on the tray. This was carried out to ensure homogeneous dried plum samples for each batch, which may be caused by uneven temperature distribution across the drying chamber. The subsequent opening of the door due to the removal of plum samples caused the drying temperature to drop to about 3-6°C with approximately 5 minutes to recover. Dried plum samples were allowed to cool down at room temperature before weighing and sugar analyses.

5.2.2 Sample Preparation for Sugar Analysis

The total weight of six plums was measured using an electronic balance (Denver Instruments, USA) which had an accuracy of ± 0.0001 g. The plums were destoned and the pulp weighed separately. The combined pulps of six plums in each batch were diluted with Milli-Q water to give a pulp:water dilution ratio of 1:5. The pulp was then homogenised with water using a mechanical blender (Panasonic). The liquefied mixture was allowed to stand for about 30 minutes before analysis. Samples were centrifuged and the extract was then filtered through a disposable Millipore 0.45 µm filter unit prior to injection onto a chromatography column. Dilution was necessary to prolong the lifetime of the column and to prevent crystallisation and build up of sugars inside the fine capillary tubings of the chromatographic system due to high concentration of sugars in plum samples. The preparation of juice for sugar analysis of fresh plum samples and the commercially produced prunes was carried out in the same manner as described.

5.2.3 High-Performance Liquid Chromatography (HPLC) Analysis

A schematic diagram of the HPLC setup together with the conditions employed in this study is shown in Figure 5.1. The chromatographic setup consisted of a column packed with stationary phase, a Knauer HPLC pump for delivering the solvent from reservoir to the column, a system for introducing the sample onto the column (Rheodyne injector), a Waters differential refractometer detector (10mV output, x8 attenuation) and a Shimadzu C-R6A Chromatopac integrator for recording the output. The integrator settings employed are presented in the Appendix section. A Waters 10µm Silica-Pak,
Radial-Pak cartridge (8mm I.D. x 100mm) for carbohydrate analysis was used in a Waters RCM-100 radial compression module. A C-18 precolumn was also connected to the system to prevent sample build up on the column. The mobile phase consisted of acetonitrile (LC grade), an amide modifier reagent (Waters SAM-1), and Milli-Q water in the ratio of 77:2:21. The solvent was then filtered through a Millipore 0.45μm nylon membrane filter unit and degassed under vacuum prior to use. Also, the mobile phase was degassed to prevent bubble formation since bubbles may cause variations in the flow rate if they reach the pump. The flow rate used was 2 ml/min. Waters “SAM-1” reagent is designed to separate sugars and related compounds using Waters Silica-Pak chromatographic cartridges.

**Figure 5.1.** Schematic diagram of the experimental HPLC system and the conditions employed.

Standard solutions of sugars used for calibration consisted of fructose, glucose, sucrose and sorbitol. Four concentrations were prepared; 3000, 6000, 9000 and 12000 ppm for each component. The standards were filtered using a disposable 0.45μm cellulose nitrate filter unit prior to injection onto the column. The volume of the sample injected was about 20μL. At least three runs were performed at each concentration and the peak areas...
for the separated sugars obtained from chromatogram were averaged. This enabled the concentration of sugars in the plum sample to be determined by comparing their peak areas to those of the standard solution. The mean concentration of sugars in the plum samples was then expressed in terms of fresh weight of plum as mg sugars/g fresh weight.

5.2.4 pH Determination

The determination of pH of fresh plum samples was carried out using a Suntex SP-31 pH probe. The method reported by Wilford\textsuperscript{14}, which gave the most reproducible results, was employed. Splitting the plum into halves and removing the stone did this. The probe was then plunged into the pulp of both halves and the pH was taken as the average of the two values. At least ten plum samples were used in each determination and the mean values were reported.

5.3 RESULTS AND DISCUSSION

5.3.1 Carbohydrate Content of d'Agen Plums

Numerous studies have shown that the carbohydrate content of plums varies with cultivars.\textsuperscript{9} Working on d'Agen variety, Wilford\textsuperscript{14} and Newman\textsuperscript{15} have found that the carbohydrates present in fresh plums are mainly fructose, glucose, sucrose and sorbitol. However, it was thought that the carbohydrate content might vary with seasons. In this study, an attempt was made to further investigate the composition of fresh plums in order to examine the natural variation of carbohydrate content of plums between seasons.

Figure 5.2 depicts a chromatogram of the juice sample extracted from the pulp of fresh d'Agen plums diluted with water in the ratio of 1:5. The figure shows four different peaks eluted at various times. Peak 1 corresponds to the fructose peak, whilst peaks 2, 3, and 4 are sorbitol, glucose and sucrose, respectively. The identification of individual carbohydrates in the plum sample was determined by comparison with the elution times of each component from standard samples. Figure 5.3 illustrates a typical chromatogram
of the standard sugar solution composed of fructose, glucose, sucrose and sorbitol with each component having the same concentration of about 12000 ppm. Clearly, the result shows a good match of the elution times of each sugar component between the plum and the standard samples confirming the identity of individual sugars in the plum sample. These results are consistent with those obtained by Wilford\textsuperscript{14} and Newman.\textsuperscript{15}

\textbf{Figure 5.2.} HPLC chromatogram of fresh plums (1) fructose, (2) sorbitol, (3) glucose and (4) sucrose.

\textbf{Figure 5.3.} HPLC chromatogram of 12000 ppm standard sugar solution (1) fructose, (2) sorbitol, (3) glucose and (4) sucrose.
Figure 5.4. Example of the standard calibration curve for glucose component.

The concentrations of individual carbohydrates present in fresh plums were quantified using the calibration curves for each component in the standard sugar solution. Figure 5.4 shows a typical standard curve for one of the carbohydrate components. The carbohydrate contents of d’Agen plums obtained from different picking seasons are shown in Figures 5.5. The values reflected in this figure were an average of at least 5 replications. The results indicate a considerable variation in carbohydrate composition of plums between seasons. In general, plum samples obtained during the 1997 season have higher total carbohydrates compared with those obtained during the 1996 season. The total sugars plus sorbitol in 1997 plums was about 16.01% whilst a value of 15.64% was obtained in 1996 plums. This is consistent with the fact that the 1997 plums were found to have much higher solid content than those plums obtained during the 1996 season. Glucose was found to be the main sugar present in plums and was higher in 1996 than in 1997 plums with the mean values of about 5.30% and 4.74%, respectively. The average sucrose and fructose contents in 1996 plums were 3.44% and 3.29%. Sucrose and fructose contents in 1997 plums were about 4.50% and 1.11% relatively higher and lower than the 1996 plums, respectively. It was also found that the sorbitol
content in 1996 plums was lower with a value of 3.61% compared with those 1997 plums of around 5.67%.

Figure 5.5. Carbohydrate composition of fresh plums obtained during the 1996 and 1997 picking seasons.

The amounts of all sugars in fresh plums obtained from this study were in the range reported by Forni et al\textsuperscript{9} for 13 different cultivars of plums. For instance, the glucose concentrations of 4.73% and 5.30% obtained from this study are in accordance with the range of 2.02-6.02% found by these workers. They also reported values of fructose, sucrose and sorbitol in the ranges of 0.7-5.45%, 1.96-6.27% and 1-5.33%, respectively. In particular, the total sugars obtained from this study (about 12.03% in 1996 and 10.34% in 1997) were in close agreement with their results specifically in d'Ente plums (most similar to the d'Agen plums) with the range of 8.89-12.4%. Similarly, in terms of glucose/fructose ratio this study obtained values of around 1.61 (in 1996) and 4.26 (in 1997) which are comparable to the values of 0.9 - 5.8 reported by the same authors. In similar studies of the same plum variety (d'Agen), Wilford\textsuperscript{14} found much lower concentrations of fructose and glucose in comparison to the amounts obtained in the
present study. For example, Wilford\textsuperscript{14} reported a value of approximately 2.9\% for sucrose which is about 0.5-1.5\% lower than the present results. She also obtained sorbitol and fructose concentrations of 4.04\% and 2.48\%, respectively. These values however are within the range found in this study. In general, the total sugars plus sorbitol obtained by Wilford\textsuperscript{14} was 2-2.4\% lower than this study. The above results indicate the seasonal variations in the carbohydrate contents of plums. Natural variations in the environmental conditions particularly during fruit development together with the different degree of ripeness during harvest might be the reasons for the observed differences. It should be noted that the amount of sugars present in the plums determines its suitability for the production of dried product and may influence the drying process as well as the quality of the final dried product.

5.3.2 Changes in Carbohydrate Content during Drying

Sugars and sorbitol are significant components found in the plums and any changes during drying and storage are crucial to the quality of the end product. In this study an attempt to monitor the change in the carbohydrate composition of plums was made with the view to determine the type and extent of degradation reactions occurring during drying.

Figure 5.6 shows an illustrative example of the change in carbohydrate composition of plums during drying as a function of time. The results depicted in this figure are those for plums dried at drying conditions of 80°C temperature, 3\% humidity and 5 m/s velocity of the drying air. The concentration of sugars was expressed in terms of mg sugar per gram of fresh weight of the whole plum. The reason for expressing the changes in sugar concentration on a mass basis of fresh plums is to avoid seeing the increase in sugar concentration due to the reducing amounts of water during drying. The other reason is because it is clear from the previous chapters that at elevated temperatures (particularly at 80°C and above) mass losses other than evaporation of water are occurring. The value of each experimental data point plotted in this figure is an average of at least two replications. In all cases, it was found that the maximum standard deviation between replicates was about ±5 mg sugar per g fresh.
Figure 5.6. Carbohydrate changes in plums during drying at 80°C (Rh=3%; V=5m/s; MC_{iwb}=66%).
It can be seen from this figure that the sucrose concentration decreases with drying time. The reduction in the amount of sucrose was more prominent at the early stages of drying particularly between 2-10 hours. Sucrose concentration of plums dried for 10 hours was found to be about 87% less than their average fresh value. At the same time as the decrease in sucrose concentration, an increase in both fructose and glucose occurred. The concentrations of these two reducing sugars then gradually decreased over the drying time. Its declining trend started after about 5-6 hours of drying. The time in which the reducing sugars begun to decrease corresponds to about 49-53% moisture loss (which is equivalent to a residual moisture content of about 50-38% in dry basis). This figure also shows the change in sorbitol as a function of drying time under the same drying conditions. The sorbitol concentration was observed to remain fairly constant up to about 8-9 hours of drying although there were fluctuations, which could be attributed to natural variation. After this period it then gradually decreased with time. This corresponds to about 54-56% moisture loss (residual moisture content of about 22-17% in dry basis).

Results from this experiment show that there are significant changes in carbohydrate contents during drying of plums. The rapid decrease in sucrose concentration, which is the predominant reaction during the early stages of drying, suggests that degradation of sucrose is occurring. It mainly involves the hydrolysis of sucrose to yield into its constituent monosaccharide units, fructose and glucose. Within the experimental error due to the natural variation of sugars within the plums, the proportionate increase in the amounts of both reducing sugars is consistent with the breakdown of sucrose. According to Candy\textsuperscript{1} the decomposition of sucrose in aqueous solution can be either catalysed by acid or enzymes. The catalytic action of enzymes in this chemical reaction was assumed to be negligible because the enzymes involved are reported to be inactivated at 40°C temperature.\textsuperscript{182} During drying at temperatures of 70°C and above it was found that the plum flesh temperature has reached more than 40°C just after about 5 minutes (Figure 2.13). It should be emphasized that the decomposition of sucrose by organic acids is minimal at pH of about 8.4.\textsuperscript{36} Lowering the pH speeds up the rate of hydrolysis. In this study, the average pH of the plums for this particular experiment was found to be 4.98 (± 0.38). This is within the range necessary to proceed the acid hydrolysis reaction. It is also known that high moisture content enhances the breakdown of sucrose. Likewise,
the initial concentration of reactant may also contribute to the reaction rate. During this period there was no evidence of other major compositional degradation reactions involving carbohydrate.

Following the hydrolysis of sucrose together with the coincidental increase in fructose and glucose, the concentrations of both reducing sugars decreased. The rapid drop in the amounts of both fructose and glucose is most likely due to the onset of Maillard reaction. It was also noticed that the concentration of sucrose continued to decrease but the rate became slower due to decreasing amount of sucrose and low moisture content. This, however, further liberates fructose and glucose, which then subsequently participate in the Maillard degradation reaction. It should be noted that sucrose is a non-reducing sugar and therefore does not participate in the Maillard reaction. It is therefore likely that the degradation due to the Maillard scheme is the predominant reaction during this stage.

Maillard is a chemical reaction in which one or more carbonyl groups of the reducing sugar react with nitrogen-containing compounds such as proteins or amino acids. Belitz and Grosch\textsuperscript{10} reported 2.3\% of N-containing compounds present in edible portion of dried prunes. The reaction is known\textsuperscript{83} to proceed effectively at temperatures greater than 50°C depending on the nitrogen-containing compounds and is favoured to occur at pH 4-7. According to Van Arsdel\textsuperscript{59} the rate of browning is also dependent on the moisture content of the material being maximal at an intermediate moisture content during drying in the range of about 15-20\% (dry basis).

The Maillard reaction can be best described by the scheme proposed by Hodge as reported by Nursten\textsuperscript{84} shown in Figure 5.7. The scheme is divided into three stages. The early stage involves condensation between the carbonyl group of the reducing sugars and the amino acid compounds to form a Schiff base. Probably, the interaction of amino compounds with reducing sugars initially involves addition of a carbonyl group to a primary amino group of an amino acid or protein, followed by water elimination leading to an intermediary imine which cyclises to a glycosylamine.\textsuperscript{10} In the case of glucose (aldose), N-substituted glycosylamine is formed from the condensation reaction, which is then converted by subsequent Amadori rearrangement to produce 1-amino-1-deoxy-2-
Fructose (ketose) undergoes similar reaction to form ketosylamine followed by the Heyns rearrangement to form 2-amino-2-deoxyaldoses. Thus the initial stage produces two intermediates, the Amadori and Heyns products. At this stage there is no discoloration or flavour production to the food system although the reaction can severely reduce nutritive value.

![Diagram of nonenzymatic browning scheme (Nursten)](image)

**Figure 5.7.** Nonenzymatic browning scheme (Nursten).

The intermediate stage comprises a reaction leading to the formation of precursors in the production of brown pigments (melanoids) which followed in three main pathways. In the first and second pathways, Amadori compounds undergo dehydration either by loss of three molecules of water to produce Schiff base furfurals or by loss of two water molecules to form reductones. The third pathway comprises of fission mainly aldolisation of the Amadori compounds, followed by Strecker degradation which is the interaction of amino acids and dicarbonyl compounds, which may be either dehydroreductones or fission products. In Strecker degradation, amino acids are...
degraded to the corresponding aldehydes with the loss of carbon dioxide. The final stage involves the conversion of carbonyl compounds (furfurals, fission products, dehydroreductones, or Strecker aldehydes) into final products of dark brown pigments with the presence of amines. This could be either a nitrogen-free or nitrogenous reaction. Sugars alone undergo several reactions that can produce similar end-products with Maillard reaction.

The product pattern formed from Maillard reaction is subject to large variation depending on the reaction conditions. In particular, the temperature, duration, moisture content (or water activity) of the system and the pH play decisive roles. The concentration and type of reactants have also significant influence on the Maillard reaction product profile. Only the reducing sugars can take part in this reaction as they provide the necessary carbonyl groups. However, the presence of sucrose may further enhance the reaction rate as it is known that at higher temperatures, the glycosidic bond of sucrose may be hydrolysed, releasing its monosaccharide constituents which can then participate in Maillard reaction in the normal way. Glucose undergoes Maillard reaction faster than fructose. Sorbitol does not take part in Maillard browning reactions due to a lack of a carbonyl group.

In the current drying experiment, sorbitol was found to be unaffected during the early stages and in some part during the decrease in fructose and glucose. It is known that sorbitol does not undergo Maillard reaction due to its lack of a carbonyl group necessary for the reaction. This further supports the idea that the Maillard scheme is the main reaction during the early part of the period in which both reducing sugars are in decreasing manner. However, after 8-9 hours of drying at 80°C the concentration of sorbitol started to decrease. Although sorbitol is not easily caramelised and that caramelisation generally requires higher temperatures, it is likely that the water activity within the prune even at this temperature (80°C) is sufficiently low enough to allow caramelisation reactions to occur.

The proportions between the reaction products due to caramelisation depend on the extent of heating, the presence of catalysts such as acid, alkalis and salts. This also
occurs when sugars are subjected to heat in concentrated solution. The color formation also depends on the type of sugar used. Kroh87 reported that caramelisation reaction requires temperature above 120°C and favours at 9 > pH > 3. The reaction can be affected by heat catalysed by acids or bases.87 The rate of caramelisation81 increases with increasing temperature and pH. Caramelisation is an ionic reaction36 that may be catalysed either by acids (at pH 2-4) or alkali (pH 9-10). The reaction causes the release of H⁺ hence altering the pH of the system undergoing caramelisation.87

The trend in the kinetics of carbohydrate change is generally in agreement with those found by Wilford14 who also studied d’Agen plums despite the fact that she obtained complete disappearance of sucrose after 4-5 hours of drying at 80°C. The difference between the present results and hers could be due to the variation in the chemical composition of the plum samples used particularly the sugar concentrations, moisture content and the pH of the plum samples. Although both samples used were obtained from the same growing area but were collected from different picking seasons. Other possible reason may be attributed to the difference in drying conditions. It should be noted that her drying experiments were conducted in a different drying system in which the relative humidity and velocity of the drying air were not closely monitored or controlled. This prompted a closer look at the carbohydrate profile during drying under various drying conditions.

5.3.3 Effect of Process Parameters on the Kinetics of Carbohydrate Change during Drying

The carbohydrate degradation reactions discussed above are known to be affected by temperature and moisture level. During drying at different conditions of drying air (i.e., temperature, humidity and velocity), it has been demonstrated in the previous chapters that the temperature and moisture content profiles within the plums varied widely. It is therefore interesting to investigate the kinetics of the compositional changes occurring in plums during drying at different drying conditions.
5.3.3.1 Influence of Drying Air Temperature

Figure 5.8 illustrates the chemical changes occurring within the plums during drying at 70°C (Rh=3%; V=5 m/s). The effect of temperature on the kinetics of chemical changes during drying of plums is exhibited between Figures 5.6 and 5.8. It is clear from the comparison between these figures that there are significant differences in the degradation reactions between temperatures. From Figure 5.8 it appears that the reducing sugars started to decrease in about 9-10 hours whilst sorbitol seemingly begun to degrade only after about 12-13 hours of drying. This corresponds to moisture loss of around 51-53% and 56-57%, respectively.

The results indicate that at 70°C there was a reduction in the amount of sucrose and a consistent increase in the amounts of both fructose and glucose as were observed at 80°C. The results also show that the course and rate of the degradation of both reducing sugars during drying varied with temperature. A significant shift in the onset of degradation of both reducing sugars was found. It is known that the decrease in the amounts of reducing sugars is an indication of the Maillard reaction. Comparison between these figures indicates that the reducing sugars started to decline much earlier at higher temperature. At 70°C it appears that the reducing sugars started to decrease about 5 hours later than at 80°C. The result is consistent with the difference in time to reach a moisture content optimal for the Maillard reaction to proceed. Maillard reaction proceeds in an aqueous solution but it occurs more readily at low moisture levels.83 The rate often reaches a maximum at some intermediate moisture content during drying in the range of 15-20% (dry basis) moisture.59 In terms of water activity (a_w), the rate of Maillard reaction was reported84 to be maximum at intermediate values of a_w of 0.5-0.8. It should be noted that drying at elevated temperatures reduces the moisture content more quickly than at lower temperature. Hence favours the Maillard reaction to proceed earlier during drying at higher temperature.

The results also show significant differences in the rates of sugar degradation occurring at different temperatures. It is clear from these figures that the degradation of reducing sugars is much faster at elevated temperature. This is in agreement with the difference in fruit temperature. Usually the Maillard reaction would quickly take place at elevated
Figure 5.8. Carbohydrate changes in plums during drying at 70°C (Rh=3%; V=5m/s; MC_{wb}=66%).
temperatures but will proceed also at normal temperatures such as during storage. With an increase of temperature\(^{36}\) of 10°C the reaction rate increases 2-3 times. According to Kroh\(^{87}\), Maillard reaction can proceed more effectively at temperatures >50°C. Duration of heating is also important. This is demonstrated by Hurrell and Carpenter\(^{183}\) who observed that in an albumin-glucose mix almost as many amino lysine groups had reacted after 30 days at 37°C (76%), as had reacted when the same mix was heated for 15 minutes at 121°C (85%).

It was also found that sorbitol decreased earlier in the profile at 80°C compared to that at 70°C. This indicates that caramelisation reaction is likely occurring at higher temperature. It appears though that at lower temperature studied (70°C) degradation reactions particularly caramelisation may be less significant due to the fact that the fruit temperature is much lower and that the amount of sorbitol is almost constant throughout the drying period.

Clearly, the temperature of the drying air imparted significant differences in the carbohydrate degradation profile. This brought about the differences in the degree of heating, which would consequently affect the time to reach lower moisture content. From the above results, it may be suggested that the thermal degradation particularly due to Maillard reaction is less significant at lower temperature as evident from the slower rate of loss of the reducing sugars. At higher temperature, the additional liberation of reducing sugars from the further breakdown of sucrose subsequently enhances the rate of Maillard reaction due to the increase in the concentrations of both fructose and glucose. It is also possible that the degradation in the last stages of drying at elevated temperature could be due to caramelisation reaction. However, the onset of both Maillard and caramelisation reactions was found to be less defined at the lower temperature. In commercial production, prunes are normally dried to 18-20% (dry basis) moisture content and subsequently stored may be for up to 1 year or more. This means that the moisture content in the last stages of drying is well within the optimal moisture range for Maillard reaction. Thus the control of temperature at the last stages of drying is crucial for the production of satisfactory dried product.
Figure 5.9. Carbohydrate changes in plums during drying at 70°C (Rh=3%; V=1m/s; MC_{iwb}=66%).
5.3.3.2 Influence of Drying Air Velocity

Figure 5.9 shows the kinetics of carbohydrate changes in plums during drying at lower velocity (T=70°C; Rh=3%; V=1 m/s). Results in this figure show a similar general pattern to the changes at higher velocity (Figure 5.8) with a decrease in sucrose and a proportionate concomitant increase in fructose and glucose. Comparison between these figures indicates a noticeable difference in the rate of sucrose hydrolysis. The rate of sucrose breakdown at an air velocity of 1 m/s was slower than those at 5 m/s. Following the rise of the reducing sugars there was a gradual drop in their concentrations until the end period of drying. It was observed that fructose and glucose started to decrease after 13-14 hours (corresponding to about 50-52% moisture loss) of drying at lower velocity which is about 3-4 hours later compared to that at the higher velocity.

![Average fruit temperature profile during drying at different air velocities](image)

**Figure 5.10.** Average fruit temperature profile during drying at different air velocities (T=70°C; Rh=3%).

The observed differences in the rates of sucrose hydrolysis and Maillard reaction between air velocities are consistent with the temperature profile of the fruit during drying. The average fruit temperature at higher velocity was found to be about 3-4°C
higher than at the lower velocity (Figure 5.10). Increase in temperature is known to accelerate the sugar degradation reactions. The variation in the onset of Maillard reaction with air velocity is also in agreement with the moisture content profile of the fruit. Drying at higher velocity reduces the moisture content more quickly hence favours Maillard reaction to proceed much earlier compared to that at lower velocity. Lower moisture content favours Maillard reaction. At lower velocity, the subsequent loss of sucrose in the later stages of drying becomes unclear as frequent fluctuations were observed. This consequently affects the trend of fructose and glucose as well. This is probably due to the natural variation between plum samples. Despite more fluctuations at lower velocity, sorbitol in both cases was found not to vary significantly throughout the drying period suggesting that caramelisation is negligible. This is supported by the fact that the moisture content is still quite high (about 26%) at the end of drying under these conditions apart from lower fruit temperature. Although there are less clearly defined reactions at lower velocity it may be suggested that the degradation reactions may be affected by the drying air velocity.

5.3.3.3 Influence of Drying Air Relative Humidity

Figure 5.11 plots the carbohydrate changes as a function of time during drying at higher humidity (30%) with velocity and temperature of around 1 m/s and 70°C, respectively. It can be seen from this figure that there is a similarity in the change of sugars and sorbitol as observed in the lower humidity experiment (Figure 5.9) although the rate and the onset of the reactions involved may be slightly different. Initially, there was the usual decrease in the amount of sucrose with proportionate increase in both fructose and glucose. The concentrations of reducing sugars then started to decline after about 14-15 hours of drying. The point at which the reducing sugars started to decrease corresponds to a moisture loss of about 48-50% (equivalent to moisture content of 53-47% in dry basis). Sorbitol was observed to fluctuate but maintained an approximate constant value until the end of drying.

Comparison between humidity conditions in terms of the changes in carbohydrate components of plums indicates some differences. The loss of sucrose appeared to be slightly higher at higher humidity condition. This may be due to a slight difference in the
Figure 5.11. Carbohydrate changes in plums during drying at 70°C (Rh=30%; V=1m/s; MC_{iwb}=66%).
fruit temperature. During drying at 70°C, the average fruit temperature at higher humidity was found to be about 2-3°C higher than at lower humidity (Figure 3.2). Increasing the temperature is known to enhance the rates of this reaction. Another important aspect of the results was the difference in the onset of the degradation of the reducing sugars. It should be noted that this phase corresponds to the period in which Maillard reaction is at play. The degradation of both reducing sugars appeared to occur much earlier at 3% RH compared to that at 30% RH. Maillard reaction is known to proceed more quickly at intermediate moisture contents (about 15-20%). The fact that the plums dried at lower humidity approached the intermediate moisture content level earlier than those plums dried at higher humidity suggests that the above result is consistent with the different levels of moisture. In both experiments sorbitol was found to remain approximately unchanged despite some variations at the beginning and end of drying due to its natural variation within the plums. This indicates that at 70°C temperature with either high or low air humidity conditions caramelisation reaction is unlikely to occur.

5.3.4 Degradation By-products

Another interesting feature is the appearance of an additional peak in the HPLC trace, which eluted shortly after the normal elution time of sucrose. Figure 5.12 shows a representative chromatogram of plums dried at 80°C for 8 hours.

**Figure 5.12.** HPLC chromatogram of plums dried at 80°C (Rh=3%; V=5m/s) for 18 hours; (1) fructose, (2) sorbitol, (3) glucose, (4) sucrose and (5) degradation peak.
Comparison of this figure with Figure 5.2 suggests that peaks 1-4 are the same components (fructose, sorbitol, glucose and sucrose) and an extra peak in the profile shortly after sucrose. This poorly defined degradation peak (peak 5) was observed to occur following the onset of the rapid loss of fructose and glucose. However, this peak was not reproducible. Its elution time was found to be inconsistent and sometimes varied in size and shape.

The earlier work of Wilford\textsuperscript{14} also showed the appearance of a degradation peak after the normal elution time of sucrose. Probably the additional peak observed from this study is similar to that obtained by her the fact that it appears almost at the same position in the sugar profile under the same HPLC conditions used. She also reported the presence of this peak in commercially packaged prunes. Attempts were made by her to identify this probably complex mixture of breakdown products by GC-MS techniques. Evidence from her analysis suggested that this peak is due to the formation of a Schiff base adduct which is a preliminary step in the Maillard reaction scheme. This further supports the supposition that the rapid decrease in the amounts of fructose and glucose in the profile is due to the onset of Maillard reactions.

5.3.5 Effect of Fruit pH on the Kinetics of Carbohydrate Change during Drying

Perhaps one of the most important factors in determining which degradation reaction might dominate during the drying of plums is pH. It is well known that rates of acid hydrolysis, Maillard and caramelisation are affected by pH variation. Attempts were therefore made to investigate the effect of plum pH on the carbohydrate changes during drying. During the scope of this study (1996-97) the pH of the plums did not vary considerably. In 1996, the average pH of the fresh plums was found to be about 4.83 (± 0.11) whilst in 1997 the fresh plums had an average pH value of around 4.98 (± 0.38). The difference is just within the experimental error due to natural variation between plums. However, in the previous year (1995) Wilford\textsuperscript{14} carried out similar studies on d’Agen plums obtained from the same growing area (Young, NSW, Australia). The pH in that batch of fruit was found to be 3.63 (± 0.21). Wilford’s drying experiments were conducted using a standard laboratory air oven. In this type of drying system only the
temperature could be controlled. Similar investigations were then carried out using the same drying system at identical drying conditions. Changes of carbohydrates during drying were also monitored using the same HPLC setup. Using these data and those obtained by her, it is therefore possible to obtain a reasonable comparison on the influence of plum pH upon the kinetics of carbohydrate change during drying.

Figure 5.13 plots the experimental data reported by Wilford\textsuperscript{14} showing the changes in carbohydrate content of plums dried at 90°C as a function of drying time (pH=3.63). It can be seen from this figure that the sucrose constituent has completely disappeared from the profile just after 2 hours of drying (equivalent to 30% moisture loss). Concomitant with the loss of sucrose there was a proportionate rise in both fructose and glucose. Following the disappearance of sucrose, the amounts of reducing sugars rapidly decreased over drying time by 2-3 hours. This corresponds to 30-40% moisture loss. Whilst the amount of sorbitol remained fairly constant up until around 3-4 hours (about 50% moisture loss) of drying time, after which it decreased over time.

![Graph showing changes in carbohydrate contents of plums with pH of 3.63 (±0.21) during drying at 90°C (Wilford\textsuperscript{14}).](image)

**Figure 5.13.** Changes in carbohydrate contents of plums with pH of 3.63 (±0.21) during drying at 90°C (Wilford\textsuperscript{14}).
The kinetics of carbohydrate change of plums (pH=4.83) during drying at 90°C are shown in Figure 5.14. This figure generally shows a similar trend to that in Figure 5.13 but the rate and the occurrence of the reactions were dramatically different. It was observed that the sucrose content also decreased as in the lower pH case but a considerable amount of sucrose left in the plum after drying to about 20% moisture content (about 9 hours). Corresponding to the loss of sucrose, both fructose and glucose increased up until 4-5 hours of drying after which it started to drop over drying time. The point in which the reducing sugars begun to decrease corresponds to about 43-50% moisture loss. The amount of sorbitol was observed to be unaffected up until 8-9 hours (61-63% moisture loss) of drying and it just slightly decreased thereafter.

![Figure 5.14. Changes in carbohydrate contents of plums with pH of 4.83 (±0.11) during drying at 90°C.](image)

The above results clearly show the effect of fruit pH on the kinetics of carbohydrate change during drying. Comparison between these results indicates that the rate of acid hydrolysis of sucrose in the present study is much slower than those obtained by Wilford. This is consistent with the pH values of the fruit. Lower pH enhances the breakdown of sucrose into its monosaccharide constituents. The results could also be
partly due to different initial concentrations of sucrose between the batches of fruit used. It was found that the plum samples used in the higher pH study contained a higher amount of sucrose than in lower pH case.

The amounts of both fructose and glucose at higher pH were also found not to decrease as much as in the lower pH case. It is known that the loss of reducing sugars is mainly due to Maillard activity. The pH of the medium is known to exert a considerable influence on the composition of the reaction products. In general, lowering the pH reduces the reaction rate of Maillard browning. Lea and Hannan found that the reaction rate was increased by a rise in pH in which it was 10 times faster at pH 7 than at pH 3. Kroh reported a pH range of 4-7 to be favourable for the Maillard reaction to proceed. Davidek et al reported that the rate of Maillard reaction increases in an almost linear fashion with the pH range of 3-8 and reaches a maximum in the alkaline range of pH in around 9-10. Foods of high acidity are therefore less susceptible to this reaction. The observed pH of the plums is therefore at the lower end of the range suited for Maillard reaction. The fact that the reaction rate at lower pH is much faster than at higher pH suggests that the effect of pH in this case may have been masked by other factors particularly the moisture content. According to Hurrell, lower pH values and high moisture appear to enhance the reaction rate in protein-sucrose systems by increasing the rate of sucrose hydrolysis rather than their influence on the subsequent reactions. It should be emphasized that Maillard reaction proceeds in aqueous solution but is favoured at low moisture contents. However, very low moisture levels retard this reaction. The initial moisture content of plums with high pH was found to be about 69% (wet basis) whilst plums with low pH was observed to have an initial moisture content of around 67% (wet basis). The earlier occurrence of Maillard at lower pH is consistent with the observed faster reduction in moisture content during drying. At lower pH, the earlier loss of sorbitol further demonstrates this behaviour and also indicates that other coupled reactions particularly caramelisation might have occurred along with the Maillard reaction. At higher pH, the slower rate of loss of sorbitol particularly at the later stages of drying might have prevented further degradation of the reducing sugars. Eichner and Kare have found that sorbitol lowers the browning rate of sugar-amino acids systems. Thus the effect of pH on Maillard reaction should be
considered in relation to other variables such as water activity and the reactant concentration.

5.3.6 Carbohydrate Content of Commercially Dried Prunes

Current commercial drying of plums involves either parallel-flow or counter-flow methods. In a parallel-flow method, the fruit enter in the hotter end of the tunnel and progress towards the cooler end. This type of drying involves exposure of the fruit to a relatively higher temperature in the early stages of drying followed by decreasing temperature until the end of drying. In counter-flow, the fruit normally experience less heating at the initial stages of drying then followed by intense heating as the drying progresses until the end of drying. Because fruit experience a different degree of heating, it would be of interest to see the final sugar composition of the prunes commercially dried at different methods.

![Figure 5.15. Carbohydrate contents of commercially dried prunes using different methods of drying.](image)

Figure 5.15 shows the carbohydrate composition of prunes commercially dried using parallel-flow and counter-flow methods. The prunes were dried down to a final moisture
content of about 18-20% (dry basis). The data are the average of at least three determinations with the standard deviation in the range of around 0.1-2.8%. It can be seen from this figure that the carbohydrate content of dried prunes varied with the methods of drying. In parallel-flow dried prunes, the total sugars was found to be about 26.1% whilst in prunes dried at counter-flow drier it was just about 21.8%. These values are consistent with those obtained for plums dried using the laboratory setup. The results show that the reducing sugars and sorbitol were generally higher in plums dried in parallel-flow than in counter-flow. Sucrose content was marginally higher in prunes dried at counter-flow.

The observed lower sucrose content of prunes dried in parallel-flow is probably because in this method of drying there may be initially a faster rate of sucrose hydrolysis. This is a consequence of the elevated temperature and higher moisture content in the early stages of drying. Higher temperature and moisture content favour the breakdown of sucrose into its monosaccharide components. The later stages of drying with low moisture content may be less favourable for sucrose hydrolysis to proceed more quickly. It can also be seen in the figure that the prunes dried in parallel-flow drier were found to have much higher concentrations of both fructose and glucose compared to those dried in counter-flow drier. The combined difference in temperature and moisture content may be the main reason for the variation in the amounts of the reducing sugars. It is known that the loss of fructose and glucose is mainly due to the Maillard reaction. Maillard reaction proceeds more quickly at elevated temperatures and intermediate moisture contents. In commercially dried prunes, intermediate moisture content is achieved normally at the end of drying. This corresponds to about 20% moisture content in dry basis (equivalent to 0.70 water activity). This means that the moisture content of the prunes at the normal end of drying is well within the moisture range optimal for Maillard reaction. The observed result in which the reducing sugars were higher in parallel-flow than in counter-flow is consistent the fact that in counter-flow drying the fruit are usually exposed to increasing temperature as they approach to the moisture range optimal for Maillard reaction. Consequently, this enhances the rate of Maillard reaction. In parallel-flow drying, the fruit approach the moisture content level optimal for Maillard reaction at a lower temperature. Thus control of the drying conditions is important in obtaining better quality-dried product.
5.3.7 Changes in Carbohydrate Contents of Dried Prunes during Ambient Storage

Dried prunes are often stored for 1 year or more before subsequent processing (rehydration) into a final product ready for consumption. It is therefore of some importance to investigate the extent of carbohydrate changes occurring during storage. This has implications on the storage stability and on the final quality of the product. The changes in carbohydrate content of dried plums during ambient storage are shown in Figure 5.16. These plums were dried down to moisture content of about 20% (dry basis) at 70°C (Rh=3%; V=5m/s). The carbohydrate composition of the plums was determined immediately after drying, then after 3 and 9 months of storage, respectively. Carbohydrate concentration was expressed in terms of percent on the basis of whole dried fruit. The data depicted in this figure were average values of at least three determinations. The standard deviation was in the range of about 0.1-1.1%.

Figure 5.16. Changes in carbohydrates of plums dried at 70°C (Rh=3%; V=5m/s) for up to 20% moisture content (dry basis) during ambient storage.
It can be seen from the results of the analyses that the sucrose content further exhibited significant loss after 3 months of storage and maintained its value thereafter. The amount of sucrose reduced from 6% down to about 2% after 3 months of storage. Corresponding to the loss of sucrose, there was a considerable increase in the concentrations of both fructose and glucose. Results show that fructose increased from 5.5% up to 7% and glucose also rose from 11% up to 12.8% after 3 months of storage. However, extended storage time subsequently decreased the amounts of both reducing sugars. After 9 months of storage, fructose reduced to 6.5% mark and glucose markedly decreased by about 2%. As a consequence, the total sugars reduced from 40.1% down to 35.3% and 33.1% after 3 and 9 months of storage, respectively. The figure also shows that there was higher sorbitol left after drying and that its concentration was fairly unchanged during storage.

The results indicate that there is further degradation of sugars during prolonged ambient storage. Significant breakdown of sucrose was found to occur during the first 3 months of storage. This is because of considerable amount of sucrose left after drying of plums down to 20% (dry basis) moisture content. During storage, the hydrolysis of sucrose could be either catalysed by enzymes or acid. The increase in the amounts of both fructose and glucose is also a clear manifestation of the hydrolysis of sucrose. Increase in the storage time to 9 months produced no further loss of sucrose. However, decrease in the amounts of the reducing sugars became the dominant reaction. It was found that the reduction in the amount of glucose was slightly higher than fructose. This is in agreement with Canellas et al\textsuperscript{187} who also observed slightly higher reduction in the amount of glucose than that of fructose during ambient storage of raisins. Hayashi and Namiki\textsuperscript{188} pointed out that glucose reactivity to Maillard is slightly higher than fructose. Hence, the decrease in the amounts of fructose and glucose could be mainly due to non-enzymatic browning (Maillard reaction). According to Davidek et al\textsuperscript{36} the non-enzymatic reactions can also take place at normal or reduced temperatures for instance during storage of foods. Non-enzymatic browning is a serious problem in the production of intermediate moisture foods. A water activity of about 0.6-0.8 makes them well within the water activity ranges for optimal browning. Prune is within this category\textsuperscript{55} the fact that its final moisture after drying is usually about 20% (dry basis) which is equivalent to a water activity of about 0.70. The constant value of sorbitol during
storage also suggests that caramelisation is unlikely to occur during storage apart from the fact that the moisture content level is not too low and that the temperature is well below the range ideal for this type of reaction. It may be implied that the deleterious changes initiated during drying continue when fruit are stored after drying. Such degradation appears to increase with storage time. From these results it may be inferred that the storage stability and quality of the dried product may be at risk and that control of the final moisture content and storage conditions particularly the temperature is necessary.

5.4 CONCLUSIONS

The carbohydrate content of d'Agen plums and their changes occurring during drying were investigated by high-performance liquid chromatography (HPLC). Plums were found to contain three predominant sugars; the non-reducing disaccharide sucrose and the reducing monosaccharide fructose and glucose. The sugar alcohol sorbitol was also detected in d'Agen plums. Glucose was the main sugar present in fresh plums. The amount of individual carbohydrates present in fresh plums was observed to vary with the picking seasons due to the natural variations between plums as a consequence perhaps of the variation in environmental conditions and the degree of ripeness during harvest.

The kinetics of carbohydrate changes during drying of plums were monitored as it has important implications on the quality of the dried product. Results from this study showed that drying induces marked changes in the concentration of individual carbohydrates present in plums. Carbohydrate changes during drying seemed to be best rationalised as a three-regime process. During the early stages of drying, acid hydrolysis of sucrose is the predominant reaction as manifested by a rapid loss of sucrose. A simultaneous proportionate increase in fructose and glucose is consistent with the breakdown of sucrose. Following the rapid rise of both reducing sugars, non-enzymatic browning (Maillard reaction) started to occur and dominate the process. This reaction is exhibited by the rapid decrease in the amounts of fructose and glucose as they react with nitrogen-containing compounds such as proteins or amino acids. The stable value of sorbitol during this period further supports the occurrence of Maillard reaction; sorbitol
is not a reactant molecule in this reaction. Further evidence of Maillard reaction is manifested by the appearance of additional peak in HPLC trace which is a possibly Schiff base adduct\textsuperscript{14} formed due to the onset of this reaction. During this regime, sucrose continues to hydrolyze but at a slower rate. Sucrose does not participate in Maillard reactions, however, its continuing breakdown further liberates fructose and glucose which can normally react then by Maillard scheme. Maillard reactions were dominant until perhaps at sufficiently extreme conditions (i.e. very low moisture content and high temperature) where caramelisation occurred (third phase). The third phase was characterised by the thermal degradation of sugar in the absence of nitrogen-containing compounds at low moisture content. At this stage the concentration of sorbitol appears to markedly decrease. This could be the indication to the onset of caramelisation reaction.

Monitoring the chemical reactions during drying at various drying conditions has a significant role to play in improving the efficiency of the drying process with better quality dried product. The course and rate of these reactions were found to be affected by the drying conditions. Temperature and moisture content of the fruit are crucial factors affecting the mechanism of carbohydrate degradation reactions. The effect of drying air temperature was found to be of great significance whilst the relative humidity and velocity of the drying air appeared less important under the range of conditions studied. The onset of the three mechanisms of carbohydrate loss was clearly defined at elevated temperatures studied (80°C and above). At mild drying temperatures (70°C), the delineation between regimes tended to be less clear. It seemed that increasing the temperature the rates of sucrose hydrolysis and Maillard reaction were accelerated. The onset of Maillard and caramelisation reactions had occurred earlier at elevated temperatures. Increasing the velocity of the drying air seemingly enhanced the reaction rates of both sucrose hydrolysis and Maillard reaction due to a slight increase in fruit temperature. The onset of Maillard reaction had also taken place earlier at higher velocity. Relative humidity of the drying air had only small influence on the rates of both sucrose hydrolysis and Maillard reaction but the onset of Maillard reaction seemed to occur earlier at lower humidity condition. Under the drying conditions studied, it was found that caramelisation was unlikely to occur except perhaps in the last stages of drying at temperature of 80°C and above when the moisture content is very low.
Differences in the rate of sucrose hydrolysis under different drying conditions studied may be also attributed to the variation of the initial concentration of sucrose between plum samples. The earlier occurrence of Maillard reaction as observed at elevated temperature, higher velocity and lower humidity conditions of the drying air is consistent with the moisture content profile of the fruit. Maillard reactions are enhanced at the lower moisture levels and achieved much earlier under these conditions.

The effect of drying conditions on the carbohydrate change was further exemplified from the carbohydrate content profile of prunes commercially dried at different drying methods. The parallel-flow method of drying plums appeared to be more suitable to obtain better quality product (high sugar content and less degradation). This is because the plums in this method of drying were exposed to reducing temperature during the last stages of drying in which they are more vulnerable to degradation (i.e., low moisture and low pH).

The scope and intensity of the chemical reactions involved during drying were found to be influenced by the pH of the fruit. The pH of the d'Agen plums was found to be within the range necessary for either sucrose hydrolysis or Maillard reaction to proceed. Results obtained from this study indicated that the kinetics of carbohydrate change were dramatically different between pH. At lower pH (3.6), the hydrolysis of sucrose was faster and had been depleted after the first few hours of drying. At higher pH (4.9), the amounts of fructose and glucose did not markedly decrease and that the onset of the reaction was delayed as in the lower pH case. This is in contrast to the normal effect of pH on Maillard reactions usually reported in literature. The influence of other factors such as the concentration of the reactants and the moisture content level might have masked the effect of pH in this case. It was also found that in the case of lower pH, the sorbitol component decreased quite rapidly and much earlier compared to that at higher pH. This might indicate coupled occurrence of Maillard and caramelisation reactions at lower pH in particular.

Because dried prunes are often stored before subsequent processing, the carbohydrate changes initiated during the drying process were followed during prolonged storage. It was found that carbohydrate composition of dried plums further degraded during
ambient storage. In the first 3 months of storage, the hydrolysis of sucrose was the dominant reaction. Further increase in storage time, Maillard reaction seemed to occur as evidenced from the reduction in the amounts of fructose and glucose. Sorbitol content was unchanged during storage indicating that caramelisation is very unlikely to occur during ambient storage of dried prunes.

It may be concluded that the high degree of complexity of the composition of plums leads to enormous diversity of chemical reactions subject to the influence of several factors. There is no doubt that the above information would be a useful tool in troubleshooting quality problems associated with production and storage of dried prunes. During the course of carbohydrate degradation, volatile flavour components may be produced. It is therefore of interest to look at the profile of volatile flavours associated during drying to further understand the underlying mechanism of the degradation reactions. This is the subject of the next chapter.
Chapter 6

IDENTIFICATION AND MONITORING OF VOLATILE CONSTITUENTS IN PLUMS DURING DRYING USING SOLID PHASE MICROEXTRACTION (SPME) IN CONJUNCTION WITH GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)
6.1 INTRODUCTION

Several studies on characterising volatile flavour constituents of different cultivars of fresh plums have been reported. These investigations have shown that the volatile compositions of plums varied substantially with different cultivars. Depending on the cultivar, esters, alcohols or aldehydes can be the major volatile constituents of fresh plums. However, these authors mentioned that among the 2000 known plum cultivars only nine have been analysed for their volatile components. It was therefore thought worthwhile investigating the volatile compositions of fresh d'Agen plums for the first time.

Most of the studies have been carried out to determine the volatile constituents of fresh plums. There has been, however, very little work on monitoring the changes of the volatile compositions of foodstuff during processing in particular during drying. The recent work of Nijhuis et al on aroma profiling during hot air drying of mushrooms provides one example on this aspect. In particular, no information has been found on aroma profiling during drying of plums. Plums of d'Agen variety are normally dried for the production of prunes due to their high solid content. During drying, water is not the only substance that escapes from the food matrix. Many constituents responsible for the aroma of food are also volatile and can readily evaporate from the product. As a consequence, the aroma characteristics of the dried product may be different. Thermal degradation processes such as Maillard and caramelisation reactions may also occur during the drying of plums as discussed in chapter 5. It has been reported in the literature that during these reactions several volatile compounds may be produced depending upon the type of the degradation process. These processes are influenced by factors such as temperature, moisture content, pH and the chemical composition of the foodstuff. Interactions between reducing sugars and amino acids or proteins have been reported to give rise to a wide spectrum of flavour compounds during heating. Therefore, identification of relevant routes leading to flavour formation particularly associated to degradation reactions has significant implications for quality control. Monitoring the changes in volatile components would also be of considerable interest to increase our understanding of thermal degradation processes during drying.
The analysis of flavours in foods generally involves extraction, concentration, separation and identification. Gas chromatography (GC) is usually the best instrument employed for separating different constituents of the extracts. Identification of individual constituents is realised by mass spectrometry. Extraction of the flavour components is a prerequisite of the analysis. In recent years, a number of methods have been developed and applied to the extraction of volatile components of plums. In most cases, conventional methods of distillation coupled with solvent extraction have been used.4,31,192 These methods have various drawbacks including the excessive use of organic solvents and time-consuming procedures. Amongst the other most widely used techniques is static headspace analysis, which involves a purge and trap method. This method is ideal for the study of flavour because it closely represents compositions, which one actually smells in foods. However, large amounts of sample are required and that the process usually involves lengthy procedures prone to leak and contamination.

Recently, a new technique known as Solid Phase Microextraction (SPME) was developed that allows easy extraction of volatile compounds.193 The technique is based on the adsorption of analytes onto a phase-coated fused silica fibre. Adsorption of the volatile components can be carried out by directly immersing the fibre into the liquid sample or exposure to the headspace above the sample. Components adsorbed to the fibre are then thermally desorbed onto a GC-MS system for separation and identification. This technique has some advantages compared to classical methods as it needs a small amount of sample and is simpler. In addition, the technique is less time-consuming and is solvent-free.

Solid Phase Microextraction (SPME) technique has been mainly applied to the analysis of pollutants in water samples.194, 195 Other reported applications of this technique include food analysis and drug studies.196 It has been successfully used for flavour analysis of fruit juices beverage, vegetable oil and ground coffee.89 In fruit juice beverage, for example, the sensitivity of SPME was found to be comparable to that of conventional solvent extraction methods for most esters and terpenoids. They also found that for ground coffee, a conventional headspace sampling method was more sensitive to highly volatile compounds while the SPME headspace method extracted more of the less volatile compounds. More recently, the SPME technique was used for the analysis
of volatile flavours in foods and beverages. The SPME technique was also applied for quantitative headspace analysis of aroma volatile production from apples during cool storage. However, its application for aroma profiling of fruit products during drying has been limited. Moreover, the choice of an appropriate type of fibre coating and the optimum extraction conditions has also to be established for a particular application.

This chapter examines the development of a micro-technique suitable for the analysis of headspace volatile components from a small quantity of sample. Changes in the volatile compositions of plums during drying were studied to identify the major volatile flavours associated with the thermal degradation processes that would provide a foundation for quality control. The technique was applied to characterise the roles of volatile flavour emission for better understanding of the thermal degradation mechanisms.

6.2 EXPERIMENTAL

6.2.1 Sample Preparation for Analysis

Flavour component analyses were carried out on fresh and dried d’Agen plums. Dried samples were prepared by drying plums using the experimental drying setup described in chapter 2. A comparison of several methods of sample preparation was undertaken to optimise the extraction process of volatile components.

Volatile analysis of whole intact and mashed plum samples was examined. A glass tube fitted with a rubber septum which accommodate 3 whole plums was used, whilst for the mashed samples ten plums for each test were utilised. These latter plums were destoned and the flesh homogenised with milli-Q water in a mechanical blender (Panasonic). Dilution with 1g of H₂O per g sample ensured a homogeneous sample and avoided difficulties of blending the dried samples. This was also necessary to enhance the effect of salting. About 25 grams of mashed plum sample were then taken and immediately transferred to a glass vial (50mL). One gram of salt was added to the vial and the sample was thoroughly stirred and quickly capped. The addition of salt is widely used to increase the sensitivity of an analytical method by changing the properties of the phase boundary and decreasing the solubility of hydrophobic compounds in the aqueous
A headspace to solid ratio of 1:1 was used to ensure that the entire length of the fibre was fully exposed without touching the sample. The sample was allowed to stand at room temperature for about 30 minutes prior to the extraction of volatiles.

### 6.2.2 Solid Phase MicroExtraction (SPME) Analysis

The extraction and injection of volatile components were made using a Solid Phase Microextraction (SPME) technique. An illustrative diagram of the Solid Phase Microextraction (SPME) device is shown in Figure 6.1. It consisted of a commercially available manual SPME fibre holder equipped with a SPME fibre (Supelco, USA). The SPME holder was made of a stainless steel barrel, plunger, adjustable needle guide/depth gauge and a septum piercing needle. Each SPME fibre assembly was fitted at the end of the plunger of the fibre holder and is equipped with stainless-steel needle. The stainless-steel needle housing the fibre allowed piercing of the septa of both the sample vial and the GC injector port. The SPME fibre assembly also composed of a one-centimetre length fused silica fibre coated with a bonded stationary phase to absorb analytes from a sample.

The efficiency of adsorption of the analytes onto the fibre was dependent upon several factors. Preliminary experiments were conducted to compare different types of fibre coatings and to optimise the extraction conditions during headspace sampling. The sample-containing vial was held at 60°C in an oven for about 1 hour to establish equilibrium between the headspace and the sample prior to SPME sampling. Blank runs were performed regularly prior to sample analysis to ensure the removal of impurities. Each new fibre was conditioned before use by a procedure recommended by the manufacturer of desorbing any material on the fibre in a GC injector port at 250°C for about an hour. Further conditioning of the fibre was made before each test in the injection port of the GC at 200°C for about 2 minutes.
The extraction efficiency of three commercially available fibres coated with different materials was investigated. Three different types of fibre coatings were tested: 100µm polydimethylsiloxane, 7µm polydimethylsiloxane and 85 µm polyacrylate. The fibre that provided the best results was used further to determine the optimal extraction conditions. The extraction conditions studied were the adsorption time and temperature. Adsorption times were varied between 10-20 minutes to further verify the effectiveness of the SPME technique. The effect of adsorption temperature on the yield of the extraction was studied at three different levels (40, 60 and 80°C).

The extraction of volatile components was carried out by inserting the SPME probe into the sample vial. With the fibre withdrawn, the needle pierced the septum of the sample vial and the plunger assembly was push down until the fiber was fully exposed. In sampling, the fiber was then exposed for a predetermined time to either the gas phase above the sample (headspace sampling) or immersed into the solution (liquid sampling) by depressing the plunger. After this, the fiber was retracted into the needle by raising the plunger so that the fibre was inside the needle before removal from the sample. After
sampling, the needle was removed from the sample vial with the extracted compounds ready for immediate GC-MS analysis.

6.2.3 Gas Chromatography - Mass Spectrometry (GC-MS) Analysis

Volatile components adsorbed onto the SPME polymeric coated fibre were thermally-desorbed onto a gas chromatography-mass spectrometry (GC-MS) system for separation and identification. The desorption of the analytes was carried out by directly exposing the fibre in the injector port of the GC for 1 minute at 200°C.

Table 6.1. Gas chromatography-mass spectrometry (GC-MS) analysis parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oven temperature</td>
<td>32 °C</td>
</tr>
<tr>
<td>Oven equilibrium time</td>
<td>0.5 min</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>200 °C</td>
</tr>
<tr>
<td>Interface temperature</td>
<td>280 °C</td>
</tr>
<tr>
<td>Sampling time</td>
<td>1.2 min</td>
</tr>
<tr>
<td>Column length</td>
<td>30 m</td>
</tr>
<tr>
<td>Column diameter</td>
<td>0.32 mm</td>
</tr>
<tr>
<td>Column pressure</td>
<td>8 kPa</td>
</tr>
<tr>
<td>Column flow</td>
<td>1.5 mL/min</td>
</tr>
<tr>
<td>Linear velocity</td>
<td>43.7</td>
</tr>
<tr>
<td>Split ratio</td>
<td>5</td>
</tr>
<tr>
<td>Total flow</td>
<td>9.2 mL/min</td>
</tr>
<tr>
<td>Mass range</td>
<td>35 - 300</td>
</tr>
<tr>
<td>GC program time</td>
<td>58.5 min</td>
</tr>
<tr>
<td>Detector voltage</td>
<td>1.7 kV</td>
</tr>
<tr>
<td>Scan interval</td>
<td>0.5 sec</td>
</tr>
<tr>
<td>Scan speed</td>
<td>500 amu/sec</td>
</tr>
</tbody>
</table>
GC-MS analysis was carried out using a GC-17A gas chromatography directly interfaced to a QP-500 quadrupole mass spectrometer (Shimadzu Corporation, Japan). A splitless injection mode was used. Separation of components was carried out on a SGE BP5 column (length: 25m; ID: 0.22mm; Film: 0.22mm). The GC column temperature was programmed as follows: initial temperature held at 32°C for 2 minutes, then increased to 250°C at a rate of 4°C/minute and finally held at 250°C for 2 minutes. Helium was the carrier gas with a flow rate of 1.5 mL/min. The pressure was held at 4 kPa for 2 minutes, then increased to 40 kPa at a rate of 0.6 kPa/minute and finally held at 40 kPa for 2 minutes. Other GC-MS operating parameters used are summarised in Table 6.1. The total time of a single run was about 57 minutes. Compounds were identified by matching their mass spectra with the data found in the library of standard compounds using computerised NSB search facilities. Mass spectrometric indentifications were further authenticated by comparison with those in the literature.

6.3 RESULTS AND DISCUSSION

6.3.1 Volatile Constituents of Fresh Plums

In this study, SPME technique was used for qualitative analysis of volatile flavours in fresh plums. Several factors have been reported to affect the sensitivity of the SPME technique including the type of fibre, sample matrix, adsorption time and temperature. In order to establish the maximum potential of the technique, a variety of commercially available fibres was examined and the extraction conditions were optimised.

In SPME headspace sampling, the extraction of the volatiles is usually influenced by the release of the analytes into the headspace, which depends on mass transfer of molecules from the sample matrix and partition between the headspace and the fibre. Mass transfer from the sample matrix is likely to be dependent on the size of the molecule, resulting in widely different adsorption efficiencies. Thus the sensitivity of the technique depends not only on the properties of the fibre but also by the mobility of the molecule within the sample matrix as influenced by the extraction conditions.
The best SPME fibre suitable for this particular analysis was determined. Each of the fibres examined was found to exhibit different affinities to analytes. No volatile flavours could be detected using the 7μm polydimethylsiloxane fibre whilst notable amounts of flavours were extracted using either the 100μm polydimethylsiloxane or 85μm polyacrylate fibres. The 100μm polydimethylsiloxane fibre absorbed more volatile constituents (8 components) than the 85μm polyacrylate fibre (4 constituents). However, the polyacrylate fibre had a higher affinity for these four components compared to the polydimethylsiloxane fibre. This could be due to the different polarities of the fibre-coat and the individual volatile component. On the basis of the results, the 100μm polydimethylsiloxane fibre, which extracted the most number of volatile constituents, was selected. Using this type of fibre, the optimum extraction temperature and exposure time were found to be about 60°C and 15 minutes, respectively. An illustrative chromatogram of headspace volatile flavours from the blended fresh plums using the optimised extraction conditions is depicted in Figure 6.2.

Figure 6.2. GC-MS chromatogram of the headspace flavour constituents of fresh blended plums extracted using 100μm polydimethylsiloxane-coated SPME fibre.
A total of 8 volatile components from fresh plums was positively identified by GC-MS analysis. A good mass spectral match with the NSB library data confirmed the identity of most of these compounds. Further authentication of the compounds was made by comparing with those found in literature. An illustrative example of mass spectral comparison is shown in Figure 6.3. The identity of the compound is also shown in figure. There were seven major volatile flavour constituents and one minor component identified.

**Figure 6.3.** Mass spectrum of hexanal in comparison with that from NSB library collection.

The first major component in the chromatogram was an unresolved peak (peak 1). The deconvolution of this peak was carried out by scanning the total-ion-current (TIC) chromatogram peak and recording the intensity of the mass peaks present in the spectrum. The identification of the components was made on the basis of mass to charge ratio (m/e). Result of the analysis showed that the unresolved peak comprised of two major components; air as a consequence of injection onto the GC-MS system and ethanol. Mass spectral comparison confirmed the identification of the alcohol. The
presence of ethanol in other plum cultivars has been well documented by several authors.29, 192, 199

Amongst the major components identified were three C₆ compounds, hexanal, 2-hexenal and 1-hexanol (peaks 2, 3 and 4). Other major volatile constituents were also detected which include octamethyl-cyclotetrasiloxane (OMCTS) (peak 5), nonanal (peak 7) and 1-(2,6,6,-trimethyl-1,3-cyclohexadien-1-yl)-(E)-2-buten-1-one (TMCHB) (peak 8). Additional minor compound such as benzeneacetaldehyde (peak 6) was also prevalent in the fresh plums.

The C₆ compounds identified (hexenal, 2-hexenal and 1-hexanol) were amongst the most abundant volatile components found here in fresh plums. These compounds have previously been shown27, 200 to be significant in the aroma of fresh plums. Enzymatic activity as a result of tissue disruption (e.g. blending) during sample preparation is thought to trigger the release of these constituents from their bound state. According to Frankel201, the presence of these compounds could be due to lipoxygenase activity, which is the reaction initialised by the disruption of the fruit tissues when blended. These flavour compounds may be also produced through the same mechanisms during the normal preparation (i.e., cutting, peeling, crushing, etc.) of fruits. Therefore they are essential to the flavour of most fresh fruits which are usually prepared in this manner before consumption and consequently can not be considered as real artifacts. The presence of these compounds in cut fresh plums was also reported in literature.27, 30, 192, 202 Williams and Ismail27- have implicated these compounds to be important to the plum aroma. For instance, hexanal when diluted has been described by these authors as having a plum-like aroma.

The relative contribution of various constituents to plum aroma was studied by Gomez et al.30 They reported that nonanal had an important contribution to plum aroma. Ismail et al29 studied the aroma components present in the headspace of four cultivars of intact plums. They found that the volatile constituents differed only in quantitative composition and that nonanal was also one of the dominant components. Ismail et al29, 93 and
Williams and Ismail\textsuperscript{27} described nonanal as a characteristic constituent of the skin waxes of plums, having a fragrant, woody-like aroma.

Except for OMCTS and TMCHB, the volatile compounds obtained from this investigation have been previously reported in the literature to be significant aroma compounds in fresh plums. OMCTS detected in this study was thought to be derived from the fibre. However, results from the fibre blank runs indicated the absence of this compound in the trace (Figure 6.4).

\textbf{Figure 6.4.} GC-MS chromatogram of the headspace blank run using 100\textmu m polydimethylsiloxane-coated SPME fibre.

The presence of other constituents during sampling may have triggered the dissociation of this compound from the fibre when used in plum samples. This is quite an interesting observation in terms of the lifetime and stability of a fibre. It was also observed that the flavour constituents obtained from this study were less than those reported by several authors. The apparent absence of some of these constituents may be due to several factors. Some of these factors could be the methods of extraction of the volatile flavour and the variety of plums used. However, the intention here was to consistently extract
major components of fresh plums with those reported in the literature using a micro-technique applicable for the analysis of small samples. This appears to have been successful showing this technique has great potential to provide a new micro-method of monitoring product quality and flavour profiling during processing.

6.3.2 Use of SPME Technique to Sample Headspace of Whole Plums

Before any further analysis, the reproducibility of the SPME technique was examined using fresh blended plum samples. Three replicate measurements were performed under identical extraction conditions. The extraction conditions used previously were employed. Each sample was prepared freshly in three separate vials. The precision was evaluated by calculating the mean, standard deviation and the relative standard deviation (%RSD) of the observed values. Results of the tests are presented in Table 6.2.

Table 6.2. Reproducibility of the headspace SPME technique from blended fresh plum samples using 100μm dimethylsiloxane fibre.

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Retention time (min)</th>
<th>Peak area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>StDev</td>
</tr>
<tr>
<td>hexanal</td>
<td>5.455</td>
<td>0.042</td>
</tr>
<tr>
<td>2-hexenal</td>
<td>7.090</td>
<td>0.020</td>
</tr>
<tr>
<td>1-hexanol</td>
<td>7.698</td>
<td>0.023</td>
</tr>
<tr>
<td>OMCTS*</td>
<td>12.125</td>
<td>0.018</td>
</tr>
<tr>
<td>benzeneacetaldehyde</td>
<td>14.164</td>
<td>0.017</td>
</tr>
<tr>
<td>nonanal</td>
<td>16.624</td>
<td>0.015</td>
</tr>
<tr>
<td>TMCHB**</td>
<td>26.359</td>
<td>0.087</td>
</tr>
</tbody>
</table>

Note:

* octamethyl-cyclotetrasiloxane
** 1-(2,6,6,-trimethyl-1,3-cyclohexadien-1-yl)-(E)-2-buten-1-one

The table shows the volatile constituents of fresh plums with their corresponding retention time and peak area. The reproducibility in terms of the retention time for all
the compounds extracted was excellent. It was found that the RSD for retention time was less than 1%. On the other hand, the reproducibility in terms of the intensity of the extracts varied with different components. Of the seven compounds extracted, four had a RSD greater than 30%. Several researchers have reported a relative standard deviation of the SPME technique in the range of about 3-30% depending upon the type of application.\textsuperscript{194, 195} The differences in the reproducibility of the SPME technique obtained from this study could be attributed to the natural variation in the composition between fruit samples.

To verify further the reproducibility of the technique several runs were made using a standard mixture of compounds known to be present in fresh plums. The compounds selected for this test include acetic acid, ethyl acetate and 2-hexanol.\textsuperscript{4} Three separate standard solutions were prepared fresh containing 10 ppm each of the above compounds. It was found that the reproducibility of at least three determinations in terms of the quantity of the extracts was less than 6%. This supports the notion that the poor reproducibility in the plum sample was caused by natural variation within the plums.

Figure 6.5. GC-MS chromatogram of the headspace flavour constituents of whole fresh plums extracted using a 100µm polydimethylsiloxane-coated SPME fibre.
In order to simplify the preparation of samples for the extraction of flavours using SPME, the method of using whole intact plum samples for headspace extraction was examined. This method was compared to that of using blended plum samples. Figure 6.5 shows the chromatogram of fresh plums extracted from the headspace of whole intact fresh plums.

Comparison between this figure and Figure 6.2 showed that there are qualitative and quantitative differences in the constituents between the two methods of sample preparation. The use of blended fruit sample in the analysis of volatile flavour was characterised by the presence of high levels of hexanal, 2-hexenal and 1-hexanol compounds. There was fewer compounds detected in intact whole plums with much lower concentrations. The absence of C₆ compounds from the headspace extract of whole intact plums supports the idea that the blending technique of preparing sample for volatile analysis was responsible for the generation of these products (probably due to enzymatic reactions during the homogenisation of the fruit tissue). Qualitative and quantitative differences in the extracts between blended and whole intact plums could also be due to the additional effect of salting. In this study, the blended fruit sample was homogenised in water with the addition of sodium chloride. Several researchers have shown that the efficiency of extraction could be improved by the addition of salt to the sample matrix.²⁰³, ²⁰⁴ Wax coating present on the skin surface of the plums which is known to be hydrophobic could be the other reason which would tend to trap the flavours within the fruit matrix. However, the detection of nonanal and TMCHB both in blended and intact plum samples indicates that these compounds are present in the fruit and not subject to enzymatic cleavage to release them. The greater amount found in the blended samples supports the idea of physical entrapment of components within the fruit.

The findings suggest that the blending technique of preparing samples for volatile analysis further enhanced the extraction of compounds with insufficient volatility. However, this method may further result in the creation of other products due to enzymatic reactions during the homogenisation of the fruit tissue.
6.3.3 Changes in Volatile Constituents of Plums during Drying

Plums are usually dried at elevated temperatures (about 70-85°C) for the production of prunes. Changes in the volatile flavour components during drying process would be expected. In this study, changes of volatile composition of plums during drying were followed using the SPME technique. Typical chromatograms of the volatile composition of plums during drying at 80°C (Rh=35%; V=5 m/s) are shown in Figure 6.6. The volatile flavours were extracted from the headspace of blended plums using a 100μm polydimethylsiloxane-coated SPME fibre. Optimum extraction conditions previously established were used. Comparison between this figure and Figure 6.2 indicates that some major changes in the composition of volatile compounds in plums have occurred during drying. The first notable difference in volatile constituents of plum detected before and after drying was the complete disappearance of C₆ compounds (hexanal, 2-hexenal and 1-hexanol). By contrast bezeneacetaldehyde, nonanal and TMCHB were retained after drying.

Another interesting feature was the formation of four new compounds during drying. The first of these compounds (peak 9 at 6.35 minutes) was found in large amounts and was identified as 2-furancarboxaldehyde (Figure 6.7). The other three compounds (3,5-diphenyl-1,2,4-trioxolane, benzaldehyde and ethyl cinnamate) were also identified, their mass spectra giving a good match with those from the NSB library database.

Some important observations can be made concerning the changes of volatile constituents of plums during drying. The first notable change was the complete loss of several major volatile components during drying. The loss of compounds might be expected during drying as it is the normal consequence of heating in conjunction with high ventilation. However, some compounds originally present in fresh plums were still present after drying. Since the flavour volatiles are generally larger than the water molecules they may not readily diffuse and are trapped within the fruit matrix during drying. The retention of these compounds after drying may be also due to their lower volatility.
Figure 6.6. GC-MS chromatogram of the headspace flavour constituents of plums dried at 80°C (Rh=3%; V=5m/s) for (a) 1 hour, (b) 9 hours, and (c) 18 hours extracted using 100μm polydimethylsiloxane-coated SPME fibre.
Theories have been proposed to explain the retention of volatile components in food during drying. These include the selective diffusion theory\(^\text{205}\), which explains retention by the lower diffusivity of the aroma compounds compared to the diffusivity of moisture in the food during drying. The other theory is the so-called microregion retention theory\(^\text{206}\), which assumes that volatile compounds are immobilised in the food matrix by a trapping mechanism. According to Saravacos\(^\text{125}\), carbohydrates are known to lock in volatile flavours. This shows that some original flavour components could be retained within the dried solid, which are responsible for the natural aroma of the product.

Perhaps the most interesting aspect of the results was the appearance of new compounds during drying. These compounds were probably generated by thermal degradation of sugars and amino acids present in plums. The onset of formation and the changes in the amounts of these compounds during drying could possibly serve as an additional indicator for quality control. It is therefore of great interest to monitor their profile as a function of time during drying.
Monitoring the changes in flavour components during drying could be an important step in identifying a benchmark for quality control and in determining the thermal degradation reactions occurring during drying. Table 6.3 presents the changes in volatile components of plums during drying at 80°C (Rh=3%; V=5m/s). Significant changes in the qualitative composition of volatile constituents of plums during drying were observed. One immediate qualitative difference detected in the volatile components during drying was the disappearance of C₆ compounds. It was found that the C₆ compounds had disappeared after 1 hour of drying. Nonanal and TMCHB were found to be consistently present throughout drying. Minor amounts of OMCTS and benzeneacetaldehyde were sometimes observed during drying.

Table 6.3. Qualitative changes in the volatile components of plums during drying (T=80°C; Rh=3 %; V=5 m/s).

<table>
<thead>
<tr>
<th>Compound name</th>
<th>R. time (min)</th>
<th>Drying time (h)</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fresh</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>unresolved</td>
<td>-</td>
<td>xx</td>
<td>xx</td>
</tr>
<tr>
<td>hexanal</td>
<td>5.50</td>
<td>xx</td>
<td></td>
</tr>
<tr>
<td>2-hexenal</td>
<td>7.10</td>
<td>xx</td>
<td></td>
</tr>
<tr>
<td>1-hexanol</td>
<td>7.72</td>
<td>xx</td>
<td></td>
</tr>
<tr>
<td>OMCTS*</td>
<td>12.14</td>
<td>xx</td>
<td>x</td>
</tr>
<tr>
<td>benzeneacetaldehyde</td>
<td>14.18</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>nonanal</td>
<td>16.63</td>
<td>xx</td>
<td>xx</td>
</tr>
<tr>
<td>TMCHB**</td>
<td>26.32</td>
<td>xx</td>
<td>xx</td>
</tr>
<tr>
<td>2-furancarboxaldehyde</td>
<td>6.36</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>10.97</td>
<td>xx</td>
<td>xx</td>
</tr>
<tr>
<td>3,5-diphenyl-1,2,4-trioxolane</td>
<td>18.99</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>ethyl cinnamate</td>
<td>29.22</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

NB:  
* octamethyl-cyclotetrasiloxane  
** 1-(2,6,6,-trimethyl-1,3-cyclohexadien-1-yl)-(E)-2-buten-1-one  
✓ found in fresh and processed plums & other fruits  
x minor peak  
xx major peak  
nf not found
During the course of drying some interesting new compounds have been formed. It was found that there were four major compounds generated during drying of plums. Each of these components was detected at different stages of drying. 3,5-Diphenyl-1,2,4-trioxolane was the first compound detected. This compound appeared after 4 hours of drying. Benzaldehyde and 2-furancarboxaldehyde were detected after 7 and 9 hours of drying, respectively. After 9 hours of drying, ethyl cinnamate was also observed.

The disappearance of C₆ compounds could be due to the deactivation of enzymatic activity; these compounds were produced mainly through enzymatic activity during the blending of the fruit. As pointed out by Etievant²⁰⁷, the formation of large amounts of these compounds is via enzymatic oxidation of linoleic and linoleic acids when fruits are crushed in air or water. In this study, plums were dried as a whole fruit and the sample for flavour analysis was prepared by mashing the dried plums in water immediately after drying. Because of the absence of these compounds in the dried sample, the enzymatic activity during the blending of fruit samples may have been deactivated as a consequence of heating during drying. Davidek et al³⁶ mentioned that materials rich in lipoxygenase enzymes could be subjected to rapid heating to deactivate this enzyme. Whilst deMan⁸⁵ showed that the grinding of soybeans carried out in boiling water instantly deactivated the lipoxygenase enzyme. The loss of these volatile compounds could also be partly explained as a consequence of heating associated with high ventilation during drying or indeed chemically changed.

Attempts were made to qualitatively follow the changes in the amounts of major components during drying. This was done by plotting the peak area of each component as a function of drying time. Figures 6.8-6.13 illustrate the histograms of the changes of the major volatile components of plums during drying at 80°C (Rh=3%; V=5m/s). For components that were originally present in fresh plums (i.e., benzeneacetaldehyde, nonanal and TMCHB), it was found that their amounts varied with drying time. The variation in the amount of nonanal showed no clear pattern with drying time (Figure 6.8).
This observation might reflect the natural variation in the chemical composition of the fruit samples which is dependent on many factors, including the maturity at harvest. TMCHB, however, did exhibit some trend. It was noted that its amount increased after 3 hours of drying then slowly declined thereafter (Figure 6.9). This compound has not been identified previously in fresh plums. Aldehydes and ketones are known to be the precursors of many heterocyclic compounds such as furans and pyrazines. Heterocyclic compounds are usually formed from thermal degradation of sugars and amino acids. It is therefore possible that the reduction in the amounts of these compounds could be due to their participation in Maillard reactions.

One important aspect of the results was the increasing amount of benzaldehyde. Benzaldehyde was first detected after about 7 hours of drying. It can be seen from Figure 6.10 that the relative amount of benzaldehyde increased with drying time. This could be due to the degradation of its glucoside precursor, amygdalin, during heating as suggested by Williams and Ismail. Amygdalin has been identified in the kernels of peach, apricot, cherry, plums and prune.
Figure 6.9. Changes in the amount of TMCHB constituent of plums during drying at 80°C (Rh=3%; V=5m/s).

Figure 6.10. Changes in the amount of benzaldehyde constituent of plums during drying at 80°C (Rh=3%; V=5m/s).
The hydrolysis of amygdalin is shown in Figure 6.11. It can be seen that the hydrolytic reaction of amygdalin produces a free sugar moiety and mandelonitrile which in turn dissociates non-enzymatically to form benzaldehyde and hydrogen cyanide.\textsuperscript{36}

\begin{align*}
\text{CH} & \text{CH} \\
\text{O— glucose - glucose} & \text{COOH} \\
\text{Amygdalinic acid} & \\
\text{Alkali} & \text{CH} \\
\text{O— glucose - glucose} & \text{COOH} \\
\text{D-mandelic acid} & + \text{NH}_4^+ \\
\text{Concentrated acid} & \\
\text{C} & \text{N} \\
\text{(R)-amygdalin} & \\
\text{Dilute acid or -glucosidase} & \text{CH} \\
\text{O— glucose - glucose} & \text{C} \equiv \text{N} \\
\text{(R)-mandelonitrile} & + \text{D—glucose} \\
\text{(Hydroxynitrile lyase)} & \text{(or gentiobiose)} \\
\text{CH} & \text{=O} \\
\text{Benzaldehyde} & + \text{HCN}
\end{align*}

\textbf{Figure 6.11. Hydrolysis of amygdalin (Davidek et al\textsuperscript{36}).}

Perhaps the most interesting feature of the results was the formation of 2-furancarboxaldehyde. This furan derivative compound was generated with an extraordinary increasing profile during drying (Figure 6.12), being first detected after about 9 hours of drying. This substance probably derived from the degradation of sugar alone (caramelisation) or in combination with amino acids (Maillard reaction) by thermal heating of the fruit. High temperatures are known to activate these reactions. Maga\textsuperscript{209} pointed out that furans are mainly formed by thermal degradation of carbohydrates and ascorbic acid and from sugar-amino acid interactions during food processing. Furans were reported to be the result of the cyclisation of sugar moiety after sugar activation and Amadori rearrangements via interaction with amine compounds.\textsuperscript{210}
The scheme of non-enzymatic browning previously presented in chapter 5 (Figure 5.7) was examined in order to elucidate the possible routes leading to the formation of 2-furancarboxaldehyde and the other new flavour compounds. The scheme can be best described by three stages. According to Hurrell and Carpenter\(^{183}\), these early Maillard reactions do not cause browning or give flavour to the food system. The intermediate stage consists of the reaction of Amadori compounds, which follow three main pathways leading to the formation of precursors for the production of brown pigments or melanoids. In the first pathway, the Amadori compound undergoes fission mainly by dealdolisation.\(^{84}\) The products of this reaction include such flavour components as acetaldehyde, pyruvaldehyde, diacetyl, and acetic acid. This is followed by Strecker degradation in which amino acids are degraded to the corresponding aldehydes with the loss of carbon dioxide. The Strecker aldehydes appear to be auxillary flavour compounds\(^{211}\), which can condense with themselves, with furfural or with other dehydration products. In the second and third pathways, the Amadori compound undergoes dehydration either by loss of three molecules of water to produce furfural or by loss of two molecules to form reductones. The final stage comprises of the
conversion of carbonyl compounds (furfurals, fission products, dehydroreductones and Strecker aldehydes) into final products of dark brown nitrogen-containing pigments. During this final stage, heterocyclic nitrogen compounds such as pyrazines, pyrroles and pyradines are produced which appeared to be largely responsible for the flavours of heated foods.\textsuperscript{83}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig613.png}
\caption{Caramelisation of glucose in acidic degradation (Hurrell\textsuperscript{83}).}
\end{figure}

It would appear that the production of flavours of heated foodstuffs is due to volatile products formed in the intermediate stage such as fission products, Strecker aldehydes and furan derivatives and in the final stage of Maillard reactions. As indicated in the figure, furan derivatives may also arise from the degradation of sugars in the absence of amino acids (caramelisation). This process proceeds under acid or alkaline conditions and is also associated with a change in flavour. This reaction is favoured at high temperature and low moisture levels. An example of a common pathway\textsuperscript{83} of the caramelisation of glucose under acidic degradation is given in Figure 6.13. The reaction first involves the formation of 1,2-enol derivatives. This is followed by dehydration to yield furan derivatives such as hydroxymethylfurfural (HMF) depending on the reaction.
conditions.\textsuperscript{87} It can be seen that the intermediates of thermal caramelisation are the $\alpha$-dicarbonyl compounds such as 3-deoxyhexosulose which give rise to the important volatile products typical for caramel flavour (Figure 6.14).

![Typical caramel aromatics (Kroh\textsuperscript{87}).](image)

It is therefore possible that the 2-furancarboxaldehyde detected during drying of plums could be either from Maillard or caramelisation reactions. Since caramelisation\textsuperscript{87} normally requires high temperature $>150^\circ$C, it may be more likely that this volatile flavour was initially formed through Maillard reactions. Its extraordinary increase in the later part of drying may be evidence of caramelisation. This may be likely given the fact the fruit had, by this stage, been heated for a long period ($>10$ hours) and that the moisture content was very low ($<15\%$ in dry basis).
It was demonstrated in the previous chapter that the onset of Maillard reactions occurs after 5-6 hours of drying under these same drying conditions as manifested from significant reduction in the amounts of both glucose and fructose. These two reducing sugars are known to be the main reactants of Maillard reactions. It is interesting to note that 2-furancarboxaldehyde was detected only after 9 hours of drying. Under the same drying conditions, the sorbitol content of the plums was also found to decrease after about 8-9 hours. The decrease in the amounts of sorbitol has been implicated to be only due to caramelisation reaction as it is a non-reactant molecule in Maillard reactions due to its lack of a carbonyl group. This indicates that caramelisation reaction may have started at this period. It was observed that the amount of 2-furancarboxaldehyde is significant especially at the latest part of drying. The increasing level of 2-furancarboxaldehyde is therefore thought to be mainly due to caramelisation reactions. This is explained probably by its origin from the degradation of sugars in an acid medium. According to Davidek et al\textsuperscript{36}, the formation of furans, particularly 2-furancarboxaldehyde, is produced by degradation of sugars in acid medium during sterilisation and storage of canned fruit products. Pons et al\textsuperscript{212} identified 2-furancarboxaldehyde as one of the major degradation products found in the aroma of caramel obtained by heating a mixture of 10 kg of sucrose, 2.5 g of citric acid and 1.7 kg of water at 195°C.

To further examine this reaction, volatile component profiles of plums dried at a lower temperature were followed. Figure 6.15 illustrates the chromatogram of the volatile extracts from the headspace of blended plums dried at 70°C (Rh=3%; V=5m/s) for 18 hours. It was found that the 2-furancarboxaldehyde could not be detected during drying at 70°C. Again, it was found that under these conditions the sorbitol content of the plums was relatively unchanged. This would imply the unlikely occurrence of caramelisation. It may be therefore suggested that the production of 2-furancarboxaldehyde during drying of plums could be mainly due to caramelisation reactions.

The degradation reactions could therefore be followed from the formation of these compounds and could probably be used for routine monitoring of product quality. However, further work should be undertaken given the fact that these compounds could
be precursors for the formation of various derivatives; its yield would depend on the rates of the subsequent reactions. Davidek et al\textsuperscript{36} pointed out that 2-furancarboxaldehyde could be used as a measure of reactions, which are usually considered to cause deterioration of the sensory quality during sterilisation and storage of canned fruit products. The generation of the above compounds is therefore relevant and could be used as an indicator of the progress of Maillard or caramelisation reactions.

6.4 CONCLUSIONS

A study on characterising the volatile flavours of fresh plums was carried out using solid phase microextraction (SPME) technique in conjunction with GC-MS. Applicability of the technique was also examined for monitoring the changes in headspace volatile constituents of plums during drying. The technique was found to be suitable for headspace analysis of a small quantity of sample. It was successfully used for
monitoring changes in volatile flavours during drying of plums. Depending on the extraction conditions, compounds appeared to exhibit different affinities for the various fibres examined involving preferential adsorption of functional group onto a specific fibre.

The investigations have established the major aromatic constituents of d’Agen plums. A total of about 8 volatile compounds was found in fresh d’Agen plums by SPME. Most of these compounds were fairly common fruit volatiles.

Drying is usually employed to produce a stable product. Improvement of the quality of the dried product requires a better understanding of the chemical degradation reactions occurring during drying. Flavour or volatile component profiling during processing is an attractive way of monitoring changes. In this study, changes of volatile constituents in plums during drying were followed in order to identify the degradation reactions that are taking place. It was observed that the drying process of plums induced modifications to the fruit aroma. Significant losses of original aromas were found during drying depending on drying conditions and new volatile compounds were generated. The formation of these volatile flavours may be due to the decomposition of sugars. These were likely formed from specific thermal degradation reactions such as Maillard or caramelisation. The volatile compounds generated as a result of chemical reactions taking place during drying would further impart aromatic flavour to the product. Thus knowledge of the formation mechanisms of volatile components could be used to optimise desirable sensory attributes. Such techniques for separation and identification of chemical constituents would greatly benefit the industry in quality control.
Chapter 7

MONITORING CONDITIONS DURING COMMERCIAL DEHYDRATION OF PLUMS
7.1 INTRODUCTION

Because the conditions of the air greatly affect the efficiency of drying as well as the final quality of the product, it is therefore of considerable importance to understand the actual conditions in which the fruits are experiencing during commercial drying. Monitoring the drying conditions is necessary to establish optimum drying conditions vital for the economic operation of the drying system. Better knowledge of the drying conditions also provides an opportunity to minimise the various kinds of quality loss or damage to the product.

The commercial drying of prunes is normally carried out in long tunnel dehydrators either in counter-flow or parallel-flow configuration. The main characteristics of drying conditions in these two tunnel arrangements are different. Details of the changes in temperature and humidity of the drying air are more complicated as the system is not in a steady-state at any time. At present, commercial practice of drying prunes in Australia uses both methods of drying. Monitoring the drying conditions inside the tunnel is not normally carried out. Usually, the drying temperature at the air inlet section of the tunnel is the only available information, which corresponds to the condition near the wall. Furthermore, there is a lack of sophistication in controlling the drying conditions particularly the relative humidity in the tunnel dehydrator. It should be noted that recirculation of the drying air provides avenues for better control of the drying conditions and energy efficiency. Bertin and Blazquez213 searched the optimum capacity for a tunnel-dehydrator of the California type of plum drying and found that recirculation of a proportion of the exhaust air improved the dryer energy efficiency. In practice the recycled air represents about 12-15% of the total volume of air recirculating in the tunnel.214 However, this requires better knowledge of the actual drying conditions inside the tunnel. Better knowledge of the drying conditions in the tunnel would also provide opportunities in the optimisation of the tunnel. For example, Kiranoudis et al215 studied the optimisation of a tunnel grape dryer using temperature and relative humidity of the drying as optimisation variables. Vagenas and Marinos-Kouris216 also employed temperature and relative humidity as optimisation variables in the optimisation of an industrial dryer for sultana raisins. This was achieved by control of fresh air and humid air and exhaust dampers along the length of the drier. Furthermore, Lee and Pyun217
showed that an optimisation technique in tunnel drying of radish can be achieved using the inlet air temperature and recycle ratio.

This chapter gives a detailed account of the design, development and testing of a simple automated device for on-line monitoring of the commercial drying conditions. The idea was to develop a continuous data acquisition system, which could be used to data-log the temperature and humidity of the drying air in the commercial tunnel driers as a function of time at different locations. The rationale of the work was to gain knowledge of the conditions during commercial drying of prunes and to demonstrate the utility of the system in evaluating the performance and efficiency of the tunnel. This plays an important role in the optimisation of the drying conditions. The aim of this part is also to provide information about commercial drying to use in conjunction with the laboratory-scale studies.

7.2 DESIGN AND DEVELOPMENT OF THE MONITORING SYSTEM

A computer-controlled data acquisition system was designed and built to continuously monitor the drying conditions in commercial prune dehydration. It allowed on-line monitoring and recording of the drying conditions spatially and temporally. Detailed descriptions of the hardware as well as the software development were presented in chapter 2. It should be emphasised that this system is the same as the monitoring system component used in the laboratory-scale dehydration unit described in chapter 2. It was only modified to eliminate the datalogging process of the sample mass via the RS232 port. Instead, a modem (optional feature) could be connected to this port to allow remote control of the system. Calibrations of the sensors were also made following the procedure described in chapter 2.

7.3 FIELD TESTING OF THE DATA LOGGING SYSTEM

7.3.1 Commercial Prune Drier: Description and Operation

Field trials were conducted to test the performance of the data logging system. The device was installed in a commercial prune dehydrator at YDP’s (Young District
Producers Co-operative Ltd.) Maimaru Central Dehydrator facility. A double-tunnel dehydrator, which could accommodate a string of 6 trolleys in each tunnel, was used. The tunnel is large enough to hold a maximum of 12 trolleys of fruit. The cross-sectional area of each tunnel is about 4.6 m². About 24 trays were stacked in a trolley. Each tray has an estimated loading area of 3.19 m². The dehydrator was operated in a parallel-flow manner in which hot air and trolleys of fruit enter at the same end of the tunnel and move in the same direction towards the other end. Air is forced into the tunnel by an axial fan. The exhaust hot moist air is partially recycled and mixed with fresh ambient air. The air was heated using a LPG gas burner regulated by a thermostat controller. Trolleys were loaded into the dehydration tunnel at timed intervals. Loading and loading process was done simultaneously. The time interval of loading/unloading between trolleys was approximately 3 hours. During the loading of a new trolley, the preceding trolley was turned around to obtain uniform drying at the same time the fruit in the trolley at the exit end of the tunnel were checked for its dryness and unloaded if necessary. During loading/unloading, the doors at both ends of the tunnel were fully opened.

7.3.2 Installation and Testing Procedure

The trials took place during the 1996 drying season. Two monitoring periods of one week each were carried out. Monitoring of the drying conditions was done only in one tunnel of the dehydrator. The conditions for both tunnels in the dehydrator were assumed otherwise to be identical based on the design configuration. The temperature and humidity of the drying air during drying were monitored at different locations in the tunnel. Figure 7.1 shows a diagram of the dehydrator tunnel with the position of the sensors. The sensors were installed within the drying tunnel using the pre-existing holes in the tunnel’s brick wall. Nine positions along the length of the tunnel were investigated. The variations in drying conditions were monitored at 3 different locations in lengthwise manner (inlet, center and outlet) with 3 varying heights (top, middle and bottom).
In addition, three locations across the tunnel were also investigated (Figure 7.2). These correspond to the positions about 5cm, 50cm and 100cm from the wall. The 5cm position was located between the inner wall side of the tunnel and the trolley, which was just outside the stream of air passing through the fruit. The 100cm corresponded to the middle of the trolley when viewed in cross-section. These positions were selected in order to obtain good representation of the entire tunnel, assuming a symmetrical configuration. Three different positions were monitored simultaneously in one complete drying cycle (approximately 18 hours). This assured homogeneous results between 3 different positions in a period because variation could be observed due to different fruit loading in each trolley. At the inlet section, the sensors were positioned in such a way that sampling of the drying air conditions was made before entry into the first trolley whilst at the outlet section the sensors were placed right after the last trolley, prior to partial exhaust/recirculation-mixing. The bottom sampling positions were located just beneath the lowest tray of fruit in a trolley. The middle and top positions corresponded
to 10 and 20 trays respectively (numbering from the bottom). Sampling in other positions not specified was made approximately between trays.

Figure 7.2. Cross-sectional position of the monitoring sensors in the tunnel dehydrator.

7.4 RESULTS AND DISCUSSION

7.4.1 Performance of the Automated Monitoring System

The computer-based online monitoring system was used continuously for two one-week trials to monitor and record the drying conditions in a commercial prune tunnel dehydrator. The monitoring system at work at Maimaru, NSW is shown in Figure 7.3. The monitoring system was found to work well throughout the trials with no technical problems. Operation was uninterrupted and did not interfere with the drying process. It was observed that the system was robust enough for use in the dehydration shed. The computer-based capability permitted the system to operate in an unmanned mode for extended time periods. Features of the system included the use of three temperature/RH sensors connected in series and interfaced to the computer. The sensors in principle can be placed anywhere in the tunnel. The typical operation of the system was to sample the
conditions at predetermined time interval and average it. It provided the operator with a multiple screen display showing the current status of the points monitored graphically and numerically.

Figure 7.3. Monitoring system at work in the commercial dehydrator at Maimaru, Young, NSW.

Figures 7.4-7.6 show typical temperature and humidity profiles of a parallel-flow tunnel dehydrator for prunes obtained using the automated monitoring system. The data reflected in these figures were monitored from the inlet, centre and outlet sections of the tunnel for three addition/removal of trolleys (about 9 hours). Normally, the duration of a complete drying cycle was about 18 hours, equivalent to six addition/removal of trolleys. Trolleys of fruit were moved one step every 3 hours. Temperature and humidity values were obtained at nine different positions along the tunnel. In this case, the sensors were positioned at about 100cm from the wall of the tunnel which corresponds to the middle position in one of the two tunnels when viewed in cross-section. The set temperature of the tunnel during these monitoring experiments was 84°C. The sensor for the control of the set temperature in the tunnel was positioned at the inlet section close to the wall (about 2-5 cm).
Figure 7.4. Temperature and humidity profiles of the drying air in parallel-flow tunnel at the inlet section 100cm from the wall (Set temperature: 84°C).

Figure 7.5. Temperature and humidity profiles of the drying air in parallel-flow tunnel at the central section 100cm from the wall (Set temperature: 84°C).
Figure 7.6. Temperature and humidity profiles of the drying air in parallel-flow tunnel at the outlet section 100cm from the wall (Set temperature: 84°C).

The results showed an approximately similar pattern of drying conditions between each drying cycle. In fact, the results obtained for longer monitoring times (greater than 24 hours) demonstrated that conditions were reproducible over longer periods. The duration of each drying cycle, which is the period between openings of both inlet and outlet doors for loading/unloading of trucks of fruit, was about 3 hours. There are several prominent features of the results that can be observed. When a truckload of fresh fruit is placed into the tunnel much of the available energy supplied by the hot air is first spent in heating up the trays and fruit. In general, there was a slow increase in temperature (about 4-7°C) in between openings of the doors of the tunnel at all positions in the tunnel except at the inlet section. Corresponding to the increase in temperature, a gradual steady decrease in the relative humidity was also found. This trend continued until the time comes to load another truck of fresh fruit. McBean et al\(^{41}\) and Gentry et al\(^{43}\) also reported similar observations. Large variations in both temperature and relative humidity between drying cycles are due to the openings of the ends of the tunnel to facilitate loading and unloading of the trolleys. The period of opening the doors and loading/unloading the
trolleys generally took about 20-30 minutes. It can be seen that it also took a substantial
time (about 30 minutes) for the drying conditions to recover. However, it should
emphasised that the profiles at 100cm from the wall cannot be used to examine the
changes in drying conditions occurred during loading/unloading. This is because the
movement of train of trolleys requires the withdrawal of sensors from that position and
hence the conditions reflected in these figures during loading/unloading are those at
about 5cm from the wall. Another important features of the results that can be directly
gleaned from the graphs are the differences in temperature and relative humidity profiles
at various heights within the tunnel particularly at the centre and outlet sections of the
tunnel. Also, the temperature of the air passing on down the tunnel dropped sharply
whilst the corresponding relative humidity increased markedly. These clearly indicate
that the conditions of the drying air (temperature and relative humidity) in the tunnel
during drying are not uniform both spatially and temporally.

7.4.2 Cross-sectional Profile of the Drying Conditions

An interesting feature of the results was the substantial variations for both temperature
and relative humidity as a function of distance from the wall. Figures 7.7 and 7.8 depict
the average values of temperature and relative humidity for the top section of the tunnel.
These values were estimated for three drying cycles during periods of closure of the
tunnel. It can be seen from these figures that there were significant gradients across the
tunnel for both temperature and relative humidity particularly at the centre and outlet
sections. It should be pointed out that the 5cm values represent a sensor reading close to
the wall of the tunnel whilst the 100cm values are those in the middle of the tunnel. At
the inlet section of the tunnel, there was very little difference in either temperature or
relative humidity as a function of distance. The results confirm that the air is well-mixed
and uniform before passage through the fruit trolleys. In addition, the observed inlet
temperature (about 83.6°C) was very close to the set temperature. The set temperature
during this experiment was about 84°C.

At the centre and outlet sections of the tunnel the drying conditions near the wall were
very different from those in the middle of the tray. It can be seen that the temperature
values at 5cm (near the wall) were very much higher compared to that at 100cm (middle
Figure 7.7. Cross-sectional temperature profile of the drying in the tunnel dehydrator (Set temp: 84°C; top section).

Figure 7.8. Cross-sectional relative humidity profile of the drying in the tunnel dehydrator (Set temp: 84°C; top section).
of the tray). In the case of relative humidity, the values obtained at the position near the wall were much lower than the values in the middle of the tray. It was found that the temperature and relative humidity values near the wall were about 80.8°C and 17% whilst in the middle of the tray the temperature and relative humidity values were 64.8°C and 40.6%, respectively. This means a reduction in temperature of about 16°C and an increase in relative humidity of 23.6% between the wall and the middle of the trolley. These data were obtained for the central section along the length of the tunnel. A similar trend was also found at the outlet section of the tunnel. The results indicate that the conditions under which the fruit are drying are very different from that indicated in the set temperature (near the wall conditions). Clearly, this shows that the readings of temperature and relative humidity near the wall do not give an accurate indication of conditions in which the fruit are drying. It appears that the fruit near the side edges of the trolleys are always exposed to more severe drying conditions compared to those at the middle. Therefore, extra cautions should be taken into consideration in using the traditional wall hung method such as dry and wet bulb thermometers to monitor the drying conditions. A more sophisticated monitoring system such as adopted here gives more extensive information and better quality data.

7.4.3 Longitudinal Profile of the Drying Conditions

The monitoring work has also found substantial systematic gradients in drying conditions along the length of the tunnel. Figures 7.9 and 7.10 illustrate the average temperature and relative humidity profiles along the length of the tunnel. Drying conditions depicted in these figures were obtained from the middle height of the tunnel at 100cm from the wall. The results show quite large gradients in both temperature and relative humidity along the length of the tunnel. It was found that there was a significant reduction in temperature from the inlet to the outlet sections. For example, at the middle of the tray (100cm from the wall) the inlet temperature was about 83.5°C whilst the outlet temperature was just around 71.2°C which results to a temperature difference of about 12.3°C between the inlet and outlet sections of the tunnel. It was also noticed that the central location along the length of the tunnel recorded similar temperatures although it was a little lower than the outlet temperature. At the same time, there was a large increase in the relative humidity from the inlet to the central position. It was found
Figure 7.9. Longitudinal temperature profile of the drying air in the tunnel dehydrator at different heights (Set temp: 84°C; 100cm from the wall).

Figure 7.10. Longitudinal relative humidity profile of the drying air in the tunnel dehydrator at different heights (Set temp: 84°C; 100cm from the wall).
that the relative humidity was increased from 15.1% (inlet) to 36% (centre) at the middle of the tray. Similar results were also observed for the top and bottom positions. It was also observed that the changes in drying conditions (temperature and relative humidity) were less at 5cm (near the wall).

McBean et al\textsuperscript{41} followed the drying conditions at the air inlet section of the parallel tunnel dehydrator and across the test truck as it moves from inlet to outlet during commercial dehydration of prunes. They recorded a temperature of around 85°C with relative humidity of 22% at the air inlet section of the tunnel (hot end). They also observed a temperature gradient across the test truck and generally found a decreasing trend of air temperature along the length of the tunnel (from air inlet to outlet). Similarly, Gentry et al\textsuperscript{43} observed a declining air temperature along the length of the commercial parallel-flow tunnel.

The above observations suggest that the drying conditions the fruit experience vary significantly along the length of the tunnel. As the drying progresses the fruit are subjected to decreasing temperature with an increasing relative humidity condition. This means that there is less intense drying at the end of the drying process. Both changes in temperature and relative humidity along the length of the tunnel are consistent with the drying process. As high temperature of the drying air passes through the bulk of high-moisture plums the temperature of the drying air would consequently drop due to several factors. Heat is lost in heating the plums and the latent heat of evaporation of the moisture. The increase in relatively humidity of the drying is consistent with the evaporation of water from the plums.

Since the temperature of the air leaving the tunnel is usually higher than the ambient temperature, a substantial saving of heat can therefore be achieved by utilising the exhaust heat in any means instead of exhausting it all at once. One possible way to recover this heat is to directly recirculate the exhaust air. However, caution should be considered as the exhaust air is usually saturated to some degree with moisture and hence the recirculation of the exhaust air would eventually decrease its drying potential. It should be recognised that as the drying air is saturated with moisture this makes it ineffective as drying agent as its capacity to hold as much moisture is reduced. Control
of the recirculation that requires precise information of the drying conditions particularly at the outlet section is therefore necessary to achieve optimum economy of the operation. In addition, control of the recirculation would provide a simple way to control the level of humidity in the tunnel. Thus information of drying conditions along the length of tunnel is important in determining the optimum length of the tunnel which is economically most effective. This is also important as the final drying conditions particularly the temperature may affect the quality of the dried product.

7.4.4 Gradients of Drying Conditions from Top to Bottom

Another important marked difference in drying conditions was also observed as a function of height of the trolley. This anomaly was more prominent particularly at the central and outlet sections along the length of the tunnel. Significant differences in temperature and relative humidity were found between heights of the trolley, designated as lower, middle and top (Figures 7.11 and 7.12).

![Temperature profile of the drying air in the tunnel as a function of height at different sections (Set temp: 84°C; 100cm from the wall).](image)

**Figure 7.11.** Temperature profile of the drying air in the tunnel as a function of height at different sections (Set temp: 84°C; 100cm from the wall).
Figure 7.12. Relative humidity profile of the drying air in the tunnel as a function of height at different sections (Set temp: 84°C; 100cm from the wall).

It can be seen that there were substantial variations in drying conditions with height of the trolleys. It was found that the temperature increases whilst the relative humidity decreases as one moves from top to bottom trays of the trolley. For example, for the centre section situated at 100cm from the wall, the temperature difference between top and bottom was about 5°C whilst the RH decreased by about 8%. Similar results were also found at the outlet section of the tunnel. At the inlet end of the tunnel, there was only a slight difference in either the temperature or relative humidity between the various heights. Again, the results clearly show that the drying condition of the air before it enters the trolleys at the inlet section is well mixed and uniform.

The temperature differences between heights would result in uneven drying. The fruit in the top trays would take substantially longer to dry compared with those near the bottom. This is consistent with the fact that during the drying period when the monitoring took place, it was found that the top three to four trays were still wet at the outlet after the complete 18 hour drying. Obviously, this required additional drying
hence would incur extra labour through reshuffling and rearrangement of trolleys and trays aside from the additional energy needed.

7.5 CONCLUSIONS

A computer-controlled monitoring system has been developed and was successfully tested to monitor the conditions during commercial drying of prunes. It was found to work well and gave detailed information of the drying conditions in the tunnel. The system is inexpensive and was completely automated in which the data could be observed in real time during monitoring. If necessary the data could also be remotely accessed via modem. It allows the drying conditions to be easily followed at various positions as the sensors may in principle be placed anywhere within the tunnel. This enables precise information of drying conditions in the tunnel to be gleaned as a function of time and position. It also provides more accurate data than conventional methods such as wet-and-dry bulb techniques.

The monitoring work has demonstrated the need to have better information about the drying conditions the prunes are experiencing. It has given useful insight into conditions in which the prunes are drying. In fact, the system was found to be useful in identifying peculiarities in drying conditions in the tunnel. Using the monitoring system, the drying conditions in the double parallel-flow tunnel dehydrator for commercial drying of prunes were established. It was found that the drying conditions in the tunnel dehydrator were not uniform either spatially or temporally. Both temperature and relative humidity varied considerably during the 3 hours period between loadings and movements of trolleys. Large gradients of drying conditions were found along the length of the tunnel (i.e. between inlet and outlet). Although uniform drying conditions across the tunnel were found at the inlet section substantial variations were obtained at the central and outlet sections. These variations were recorded between the middle and near the wall positions. Further significant changes in drying conditions were also noted between the top and bottom of the tunnel. The variations in drying conditions across the tunnel dehydrator may be artifacts of this particular dehydrator. Consistent differences in dryness were found between trays of prunes depending on their position on a truck. The top few trays from an exiting trolley were usually being underdried. This demonstrates
the usefulness of the monitoring system as a tool in tunnel optimisation and management. It is simple and requires little maintenance and may easily be modified for in-line control of the drying conditions.
Chapter 8

GENERAL CONCLUSIONS
The present study was conducted in order to further our understanding of the mechanisms of moisture loss and chemical changes occurring during drying of plums. To accomplish this, an extensive investigation on the physico-chemical aspects of the drying process of plums was considered. A computer-based drying system was designed and built to investigate the kinetics of drying plums under controlled conditions. The experimental system enabled the drying experiments to be simulated in a range of conditions similar to those in a typical commercial dehydration tunnel.

**Effect of the Experimental Variables**

The kinetics of drying plums were studied under different conditions of the drying air such as temperature, velocity and relative humidity. This was carried out to ascertain the major factors controlling the drying process and elucidate the drying mechanism. Results of the study showed that the process parameters greatly affected the drying kinetics of plums. It was found that the temperature of the drying air has the most remarkable effect on the drying process. Increasing the drying air temperature was seen to be advantageous in reducing the apparent drying time. However, the use of much higher temperatures (90°C and above) may not be plausible inasmuch as severe skin splitting of plums was noted to occur. Further evidence was also obtained suggesting that some alterations in the chemical composition of the fruit might have occurred during drying at elevated temperatures. Another interesting feature was the substantial variation in the drying behaviour between 60°C and the higher temperatures. This observation could be attributed to the efficiency of cell disruption at the skin layer induced by drying. Slower rates of moisture loss during drying at lower temperatures could be due to restricted moisture movement through the skin layer under these conditions.

Other process parameters were found to impart notable effects on the drying kinetics of plums. The velocity of the drying air was found to exhibit a profound effect particularly on the initial rates of drying. However, further increase in air velocity did not result in any worthwhile improvements. In fact there was little difference in terms of the total drying time recorded during drying between air velocities of 2 m/s and above. Relative humidity of the drying air was also observed to influence the drying kinetics of plums. It
would appear from the results that drying under lower relative humidity condition is more conducive to enhance the drying process. Hence, decreasing the humidity of the drying air can significantly increase the production throughput. The results show variations in the kinetics of moisture loss during drying over the range of conditions studied and clearly highlight the need for better control of the conditions during commercial drying of fruit.

**Water Permeability Studies**

The drying process of high-moisture foodstuffs may be governed by different restrictions to moisture transfer. Usually, the external resistance prevails at the early stages of drying. This is characterised by the rate of moisture evaporation from the fruit surface to the drying air. When all the moisture at the surface is completely depleted, the rate of internal moisture diffusion may predominantly control the drying process. In waxy fruits like plums, the mechanism of internal moisture movement may be either controlled by the rate of moisture transport through the skin layer or by the diffusion within the fruit matrix. This may be due to the differences in the micro-structural characteristics between the skin layer and the underlying tissues.

Ancillary studies were conducted to elucidate this phenomenon. The permeability of water through the skin layer of the plums was determined using a radiotracer method. It was then compared with the movement of water within the fruit matrix obtained by Back and Price\textsuperscript{105} using NMR techniques. This suggested a remarkable difference in the rates of moisture transport between the skin layer and within the fruit matrix at different stages of drying. The rate of water movement through the skin layer was much slower particularly at the initial stages of drying compared to the rate of water diffusion within the fruit matrix. The permeability of water through the skin layer was observed to increase whilst the diffusion of water within the fruit matrix was increasingly hindered as the drying progressed. Transport through the skin layer is the controlling mechanism in the early stages of drying. Perhaps this phenomenon might depend on the efficiency of disruption of the waxy skin layer. At the later stages of drying the mechanism of water diffusion within the fruit matrix emerged to be the governing factor. In a parallel experiment, a relatively faster rate of drying plums without skin compared to those with
skin intact further corroborated the observation. The results suggest a more complex internal transport of moisture during drying of plums and show that the drying of plums may be controlled by several mechanisms at different stages of drying depending upon the drying conditions.

**Modelling the Drying Process**

To elucidate further the mechanisms of moisture transfer involved during drying of plums, two mathematical models were developed and tested against the experimental data. Each of the proposed models adopted different mechanisms of drying. The first model embraced the concept of two regimes of drying. The two-regime model assumed two major periods occurring during drying in which the extent of each period depended on the drying conditions. The first stage was represented by a constant-rate period where the rate of water evaporation from the fruit surface (or near the fruit surface) to the drying air is the limiting factor. This is followed by a falling-rate period in which the rate of water diffusion through the fruit matrix controlled the drying process. The falling-rate period was described only by a single phase. Parameters required in the model were estimated from the fruit temperature profile. A good match between the experimental and the predicted values connoted the suitability of the proposed two-regime model in describing the drying process of plums particularly at moderate conditions. It also validated the assumption of the presence of constant period when there is plenty of moisture available at or near the surface of the fruit as realistic for plum drying. The results further implied that the use of fruit temperature profile in estimating the parameters necessary in the model was appropriate. The model is simple and relies on few parameters. However, at extreme condition particularly elevated temperatures the two-regime model is limited. It appeared that during drying at higher temperatures (80°C and above) the two-regime model is inadequate to describe the drying curves.

To address the limitations of the two-regime model, a second drying model was formulated by considering the diffusion of water through the fruit explicitly. In this model the drying process of plums was assumed to occur entirely during the falling-rate period. It considered the drying process to follow a diffusion-like mechanism driven by
concentration gradients. The internal resistance to moisture transfer was assumed to be uniformly distributed throughout the fruit and that the effective diffusion coefficient ($D_{\text{eff}}$) was taken to be independent from moisture content and dimensional characteristics of the plums. Under these circumstances, the drying process of plums was modelled using the Fick's law of diffusion. To account for shrinkage, a numerical solution to the diffusion equation using a finite difference method was adopted. Comparison between the predicted and the experimental values showed a good agreement at 80°C. The assumption of $D_{\text{eff}}$ being independent from moisture content and the characteristic dimensions of the plums was found to be realistic. It showed that $D_{\text{eff}}$ varied with the drying temperature according to an Arrhenius-type relation. The consideration of a second $D_{\text{eff}}$ representing the initial heating stage of drying was found to improve the predicative potential of the model. The results indicated that under the extreme drying conditions the internal resistance to moisture transports mainly controls the drying process. However, the diffusion model was found to be inadequate in predicting the moisture loss process at moderate drying conditions (70°C and below). A significant difference between the predicted and experimental values was observed particularly at the early stages of drying. It showed that the drying rate was initially over-predicted. This was perhaps due to the considerable resistance imposed by the waxy skin layer to moisture transfer under these conditions. A good fit of the model with the experimental data for plums without skin under the same drying conditions further confirmed the role of the skin layer.

The proposed models predicted well the drying kinetics of plums but were applicable to different drying conditions. The modelling approach indicated that there might be different mechanisms of moisture transfer involved during drying of plums. Drying under moderate conditions seemed to be mainly controlled by the resistance to water movement through the waxy skin layer. At extreme drying conditions particularly at higher temperature and velocity, and lower humidity condition, the drying process of plums may be fairly described by the internally controlled diffusion mechanism. Generally, the proposed models could serve as descriptive tools in predicting the drying kinetics of plums. This has great utility for the optimisation of the process and in devising an efficient system of drying.
Pre-treatment to Enhance the Drying Process

Other means of enhancing the drying process of plums were explored such as using a drying emulsion prior to drying. Drying emulsions based on fatty acids/aqueous alkaline potassium carbonate are currently employed in the commercial production of sultanas. It is a chemical pretreatment intended to disrupt the water permeability of the skin layer for waxy fruits. The application of the drying emulsion in plum drying was thought worthwhile investigating as there was evidence from this study that shows a significant restrictive effect of the waxy skin layer to moisture transfer. Hence this study might further disclose the role of the skin layer in the moisture loss process during drying.

The effects of various pretreatment emulsions previously used for grapes and other waxy fruits were investigated. The study unveiled a significant effect of dipping emulsions on the drying kinetics of plums. It was found that the dipping pretreatment was mainly effective at the early stages of drying. This is consistent with the skin layer providing considerable resistance to moisture transfer at this stage. Ethyl oleate was found to enhance the drying process most. It was observed, however, that the inclusion of potassium carbonate to the aqueous dips did not significantly alter the drying process.

Further examinations of the effects of dipping pretreatment on drying of plums were made. Specifically, a commercial drying oil known as “Voullaires oil” commonly used for grapes was studied. The effectiveness of this emulsion was then evaluated under different drying conditions to explore its maximum potential in plum drying. Analysis of the results showed the commercial dipping emulsion to be less effective compared to the pure ethyl oleate based dip. The performance of the commercial drying oil in terms of enhancing the drying process was observed to vary with drying conditions. At higher temperature the drying emulsion was found to be ineffective. Perhaps the results might indicate a substantial disruption of the skin layer during drying at elevated temperatures leaving the skin’s water-barrier properties inefficient. This conforms to the modelling results the fact that at elevated temperatures the drying process may be mainly controlled by the rate of water diffusion within the fruit matrix. At lower temperatures the skin layer was implicated to be rate controlling for moisture transfer particularly in the early stages of drying. Hence a large effect of dipping pretreatment was obtained.
under these conditions. Other drying conditions such as higher air velocity and lower relative humidity were observed to be more conducive to obtain greater effect of the dipping pretreatment. This seemed to imply a significant effect of the waxy skin layer to water transport during drying.

Because the dipping pretreatment generally showed some encouraging advantages under simulated laboratory conditions, further tests were carried out in the commercial-scale level. Results of the test indicated no clear advantage of utilising dipping pretreatment under the current parallel-flow method of drying prunes because this method of drying employs initially higher temperature. This is in accordance with laboratory experiments. It is expected that the dipping pretreatment procedure would be economically beneficial under the current counter-flow dehydration because this method of drying utilises initially lower temperatures. A relatively easy way of incorporating the dipping procedure into the current practice was noted the fact that fruit are usually washed prior to drying. It showed that any problems of disintegration during rehydration are unlikely to occur and that there was very little chance of chemical contamination either in the product or in the processing equipment.

**Carbohydrate Changes during Drying**

Quality of the product is one of the major concerns during processing and storage. This is because there may be considerable alterations in the chemical composition of the material during processing and subsequent storage. A greater understanding of the many chemical reactions, which occur particularly during drying and subsequent storage, would provide a better opportunity to optimise the quality of the product. Changes in the chemical constituents of plums were therefore monitored during drying and storage.

In this study the carbohydrate contents of d'Agen plums were examined by HPLC. The results of the analysis revealed that fructose, sorbitol, glucose and sucrose are the main carbohydrates present in fresh plums. Glucose was found to be the major sugar constituent. The concentration of the individual carbohydrates present in fresh plums was observed to vary with picking seasons. This seemed to be associated with the
natural variations in environmental condition between seasons and the difference in the
degree of ripeness during harvest.

The kinetics of changes in the main carbohydrates present in d'Agen plums were
followed during drying in order to ascertain the occurrence of chemical degradations.
Results of the study showed significant changes in the amount of individual
carbohydrates present in plums during drying. It was noted that during drying several
chemical reactions might be identified corresponding to the onset of a particular
reaction. This may be best rationalised in three major schemes. Initially, there was a
dramatic decrease in the amount of sucrose with concomitant increase in proportionate
amounts of both fructose and glucose. This indicates that the degradation of sucrose by
acid hydrolysis was the predominant reaction at the early stages of drying. The second
stage was mainly characterised by the degradation of monosaccharides via Maillard-type
reactions. During this time, a rapid decrease in the amounts of fructose and glucose was
observed as they react with nitrogen-containing compounds such as proteins or amino
acids. By contrast, there was little change in the amount of sorbitol. Sorbitol is known
not to participate in Maillard reactions since it lacks the necessary carbonyl group.

Further evidence of the occurrence of Maillard reactions was exhibited by the
appearance of an additional peak in the HPLC chromatogram corresponding to this
period. This peak has been identified as a Schiff base adduct being formed as an early
product of this complex reaction. Also, at this stage the sucrose constituent continued to
hydrolyse liberating fructose and glucose which subsequently react then by Maillard
activity. It seemed that Maillard reactions continue to dominate perhaps until the last
stages of drying where caramelisation probably started to become apparent. Although
the thermal degradation of sugar alone generally requires higher temperatures, this
reaction might occur in the latter stages of drying when the amount of moisture in the
plums is very low. In the last stages of drying, the amount of sorbitol appeared to
decline, which could be a further manifestation of the onset of caramelisation reaction.

Control of the product quality requires more knowledge about the mechanism of the
effects of process conditions. In an attempt to appraise the factors affecting the
degradation reactions, the kinetics of carbohydrate changes during drying at different
drying conditions were monitored. The study revealed substantial variations in the onset
and rate of the carbohydrate degradations between different drying conditions. Temperature, velocity and relative humidity of the drying air were found to influence the mechanism of carbohydrate degradations. The effect of drying air temperature was seen to be the most obvious whilst the relative humidity and velocity of the drying air had a little impact on these reactions. At elevated temperatures (80°C and above) the onset of different carbohydrate degradation reactions was clearly defined whilst at lower temperature (70°C) the delineation between regimes of degradations was unclear. Increasing the drying air temperature appeared to enhance the rates of sucrose hydrolysis and Maillard reaction. Maillard reaction occurred earlier at higher air velocity. The relative humidity had a slight influence on the rates of both sucrose hydrolysis and Maillard reaction. However, the onset of Maillard reaction seemed to proceed earlier at lower humidity condition. In all cases, caramelisation was unlikely to happen except perhaps in the last stages of drying at 80°C and above when the moisture content of the plum is very low.

The variation in the rates of carbohydrate degradation under different drying conditions could be attributed to the differences in fruit temperature under various drying conditions. Sucrose hydrolysis and Maillard reactions are known to proceed more quickly at elevated temperatures. Whilst the variations in the onset of Maillard reactions at different drying conditions are consistent with moisture content profile of the fruit. This was demonstrated from the results the fact that the onset of Maillard reaction occurred much earlier during drying at elevated temperature, higher velocity and lower relative humidity conditions consistent with the rapid reduction in the amount of moisture in the fruit during drying under these conditions. Maillard activity is usually enhanced at lower moisture levels. During drying at mild conditions, the lower moisture content was achieved later. It is therefore important to control the drying conditions in order to obtain the desired quality of the product.

Significant differences in the carbohydrate content of prunes commercially dried using different methods of drying exemplified further the effect of drying conditions. Plums dried in parallel-flow method of drying appeared to have higher sugar content compared to those dried in counter-flow method. This means that plums dried by parallel-flow might have experienced less degradation of sugars than those dried in counter-flow. This
is because in the parallel-flow method of drying the plums were exposed to lower temperatures during the last stages of drying in which they are more vulnerable to degradation due to lower moisture and pH.

Plum pH is one of the important factors in deciding which reaction might dominate at any stage during drying. In this work, pH of the plum was found to affect the chemical reactions involved during drying. It was observed to be within the range necessary for either sucrose hydrolysis or Maillard reactions to proceed. There was a dramatic difference in the carbohydrate content profile between pH during drying. Sucrose hydrolysis was faster and had been depleted in just few hours during drying of plums with low pH (3.6). Whilst the Maillard reaction during drying of plums with high pH (4.9) appeared to be slower and had occurred later as in the lower pH. It was also found that the sorbitol component decreased quite rapidly and much earlier during drying of plums with lower pH than those plums with higher pH. This shows that the pH exerts considerable influence in the chemical degradations occurring during drying of plums.

Dried prunes are often stored before any subsequent processing. The carbohydrate changes during storage were then followed to establish the important reactions that are taking place during this period. The carbohydrate content of dried prunes was shown from this study to degrade further during ambient storage. It was found that during the first three months of storage the hydrolysis of sucrose was the dominant reaction. The amounts of both fructose and glucose were observed to decrease during the prolonged storage period suggesting the occurrence of Maillard activity. Sorbitol component was unchanged indicating that caramelisation is very unlikely to proceed during ambient storage of dried prunes.

The approach of monitoring the chemical compositions during processing and storage was shown to be very useful in detecting the progress of the chemical degradations that are occurring. It shows that the degradation reactions can be minimised by informed selection of drying conditions. The results generated from this study would certainly be of interest to the optimisation of the drying process so as to ascertain better quality product. It is known, however, that the decomposition of carbohydrates would lead to the formation of wide spectrum of volatile flavours. Flavour profiling would certainly
provide further avenues to discern the mechanism of the degradation reactions associated with the drying process. Aroma constituents in foods are extremely complex because they comprise compounds that span broad ranges of volatility and polarity. This requires precise methods for the analysis of these compounds.

**Volatile Change during Drying**

A solid phase microextraction (SPME) technique in conjunction with GC-MS was employed in this study to characterise the volatile flavours in plums. It was applied to monitor the changes in headspace volatile constituents of plums produced during drying. The novel technique was found to be suitable for headspace analysis of small quantity of sample and was successfully used for monitoring the changes in volatile flavours during drying of plums.

The major aromatic constituents in plums were identified using the approach. A total of 8 volatile flavours was found to be present in fresh plums. Most of these compounds were reported to be common in fruit. The investigations also indicated significant modifications to the aromas of plums during drying. Substantial losses of the original volatile flavours were recorded. During the course of drying, there were formations of new volatile compounds, which were thought to impart the aromatic flavour of the dried product. These compounds were implicated to be due to the decomposition of carbohydrates and were probably formed from specific thermal degradations such as Maillard and caramelisation. This demonstrates that the flavour profiling approach could be used to further diagnose the progress of chemical reactions. Hence, the insight gained through the study of flavour profiling can be used to design the drying operation so as to achieve the desired quality of the product.

**Monitoring Conditions in a Commercial Drier**

It is clear from this work that the process efficiency and product quality are greatly influenced by the drying conditions. This indicates a need for a better control of the process conditions during drying. An understanding of the actual conditions in which the prunes are experiencing during the commercial dehydration is therefore important.
This is because it is through adequate knowledge of actual drying conditions that optimum drying process can be established.

In this study a computer-controlled data acquisition system was developed to monitor the conditions during commercial drying of prunes. The rationale of the work was to obtain better information of the drying conditions during commercial drying of prunes. It was also envisaged to demonstrate the utility of the device in assessing the performance of the tunnel dehydrators.

The monitoring system was successfully tested under commercial drying conditions and was found to work well. It was completely automated in which the data could be observed in real time during monitoring and could also be remotely accessed via modem if necessary. In principle the system allowed the drying conditions to be followed at various positions as the sensors may be placed anywhere within the tunnel. This gives a more precise information of the drying conditions in the tunnel to be gleaned compared to the old methods such wet-and-dry bulb techniques. Also, the need to have better information about the drying conditions during commercial drying of prunes was demonstrated from this work. The monitoring work provided invaluable insight into the drying conditions in which the prunes are drying. In fact, the system was found to be useful in identifying anomalies in drying conditions in the tunnel dehydrator. This demonstrates the usefulness of the monitoring system as a tool in tunnel management. It shows the importance of establishing the actual drying conditions for the optimisation process.

**General Comments and Future Directions**

The overall results from this work have generated a new perspective in understanding the drying process of plums, demonstrating a physico-chemical approach of studying the drying process to be useful in devising a scientific basis for suggesting improvements to the commercial operations. There is no doubt that the results from this work could easily be extended to other fruits and products of similar characteristics. As a consequence, this would benefit the drying industry.
However, there are still some issues that need to be addressed further. The approach of unmasking the changes in the microscopic structure associated with drying could be a challenging matter to pursue. This should widen our understanding of the mechanism of internal moisture transport and may provide more information on the quality of the product. Other fascinating area such as the moisture content profiling within the fruit at different stages of drying using NMR techniques may be worthwhile investigating for better prediction of the drying process and product quality. Future studies of looking practical means of applying the pretreatment (i.e. spraying) would further substantiate a commercial realisation of this procedure. Other ways of disrupting the waxy skin layer should also be examined to reduce the drying time. Finally, a work on flavour profiling particularly for other foodstuffs using SPME is encouraged to broaden its application.

Now that the momentum for technological innovations is proceeding at a rapid pace, we may look forward to the additional information on these aspects in the near future. This should expand and fully strengthen the scientific basis contained in this work for making firm recommendations as to the revision of the drying protocol in the commercial production of prunes.
REFERENCES


References


References


APPENDIX
Appendix 2A.1 Temperature calibration curve for Vaisala probe.

Appendix 2A.2 Relative humidity calibration curve for Vaisala probe.
Appendix 2A.3 Calibration curve for the skin permeability experiments.

\[ y = 8E+07x + 133.83 \]
\[ R^2 = 0.9887 \]

Appendix 5A.1 Integrator setting used for HPLC analysis.