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**Highly selective molecularly imprinted polymer
(MIP) based sensor for fruit maturity determination**

By

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This thesis is dedicated to my family;
My parents, my wife, kids and newborn baby.
This is for you.

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TABLE OF CONTENTS

	PAGE
THESIS DECLARATION	i
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iv
LIST OF FIGURES	xi
LIST OF TABLES	xvi
LIST OF ABBREVIATIONS	xvii
ABSTRAK	xx
ABSTRACT	xxi
CHAPTER 1 INTRODUCTION	
1.1 Introduction	1
1.2 Maturity Determination	3
1.2.1 Conventional Methods	4
1.2.2 Modern Methods	5
1.3 Problem Statement on Existing Volatile Sensing	7
1.3.1 Low Selectivity	7
1.3.2 High Temperature Operation and Power Consumption	7
1.3.3 Complex Array of Sensor Combination and Complex Circuitry	8
1.3.4 Bulky and Difficult to Miniaturize	8
1.4 Research Objective	9
1.5 Significance of the Research	11
1.6 Organization of Thesis	12

CHAPTER 2 LITERATURE REVIEW

2.1 Olfaction- The Sense of Smell	14
2.2 Types of Gas Sensing Technologies	15
2.2.1 Optical Gas Sensor	16
2.2.1.1 Surface Plasmon Resonance	17
2.2.1.2 Fluorescence	18
2.2.2 Gravimetric Gas Sensor	18
2.2.2.1 Quartz Crystal Microbalance	19
2.2.2.2 Cantilever	21
2.2.2.3 Surface acoustic wave	21
2.2.3 Electrochemical Gas Sensing	22
2.2.3.1 Chemo-resistive Sensor	22
2.2.3.2 Metal Oxide Sensors	23
2.2.3.3 Conducting Polymers	24
2.2.4 Metal Oxide Sensors Field Effect Transistors	24
2.3 New Sensing approach	25
2.3.1 Molecularly Imprinted Polymer	25
2.3.1.1 QCM-MIP based Sensor	26
2.3.1.2 Chemicapacitive MIP sensor	28
2.4 MIP for Gas Sensing	30
2.5 Development of Artificial Olfactory Sensing System	33
2.5.1 Electronic noses	33
2.5.2 E-nose application for fruit maturity determination	34

CHAPTER 3 EXTRACTION AND GAS CHROMATOGRAPHY ANALYSIS OF MANGO VOLATILE

3.1	The Changes in Mango Aroma/Volatiles	36
3.2	Analysis Method for volatile detection	37
3.2.1	Gas chromatography	37
3.2.2	Mass Spectrometer	38
3.2.3	Gas chromatography mass spectrometry (GC-MS)	39
3.2.4	Solid Phase Microextraction (SPME)	40
3.3	Selection of Mango and Chemical	42
3.3.1	Determination of Mango Maturity	42
3.3.1	Chemicals	43
3.4	Experimental setup	43
3.4.1	Mango Handling and Selection Process	43
3.4.2	Solid-Phase Micro Extraction from Mango	44
3.4.3	Experimental GS-MS Setup for Identification of Mango Volatile	45
3.4.4	Calibration Curves	46
3.5	Result and Discussion	47
3.5.1	Extraction of Volatile for Harumanis Mango using SPME	47
2.5.2.1	Analysis of Volatile Extraction for Different Harumanis Mango Maturity Stages	47
2.5.2.2	Statistical Analysis of Harumanis Volatiles Emission	50
3.5.2	Analysis of Volatile Vapor over Incubation Time (Ripe Harumanis Mango)	54
3.5.3	Analysis of Volatile Vapor for Different Sala Mango Maturity Stages	55
3.5.4	Analysis of Volatile Vapor for Different Chukanan Mango Maturity Stages	58
3.5.5	α -pinene, γ -terpinene and terpinolene Calibration Curve	61

3.5.6	Analysis of Volatile Extraction Between Ripe Mango Flesh and Skin (Harumanis) using Headspace	64
3.6	Summary	65
CHAPTER 4 MIP MOLECULAR MODELLING, SYNTHESIS AND PHYSICAL CHARACTERIZATION		
4.1	Molecular Imprinted Polymer Introduction	67
4.1.1	Functional Monomer of MIP	68
4.1.2	Cross-linker of MIP	69
4.1.3	Templates	69
4.2	MIP Sensor Fabrication Development	69
4.2.1	Interdigitated Electrode	70
4.2.1.1	IDE Mask	70
4.2.1.2	Interdigitated Electrodes Fabrication by Physical Vapor Deposition	70
4.2.2	Quartz Crystal Microbalance	72
4.3	Pre-treatment of IDE and QCM crystal	72
4.4	MIP Preparation	72
4.4.1	Computational Modelling and Binding Energy Calculation	72
4.4.2	Optimization of MIP ratio composition	75
4.4.3	MIP Synthesis	76
4.4.4	MIP Deposition and Sensor Coating	76
4.4.5	Template Removal	77
4.5	Physical Characterization methods	78
4.5.1	Energy-dispersive X-ray spectroscopy (EDX)	78
4.5.2	Scanning Electron Microscopy (SEM)	79
4.5.3	Atomic Force Microscopy (AFM)	79
4.5.4	Measurement of the Thickness of the MIPs Films	79

4.6 Results and Discussion	80
4.6.1 Computational Modelling and Binding Energy Analysis	80
4.6.2 Optimization of MIP Ratio Composition	83
4.6.3 Physical Characterization Analysis	85
4.6.3.1 SEM Analysis on Fabricated IDE	85
4.6.3.2 Analysis of MIP Thin film Thickness	87
4.6.3.3 Analysis of MIP Surface Morphology	87
4.6.3.3.1 SEM	87
4.6.3.3.2 AFM	88
4.6.3.3.3 EDX Analysis	89
4.6.4 QCM-MIP Sensor Response : Frequency shift	90
4.6.5 IDE-MIP Sensor Capacitance Shift	91
4.6.6 Analysis of IDE Dimension Effect	93
4.7 Summary	94
CHAPTER 5 ELECTRICAL CHARACTERIZATION OF MOLECULAR IMPRINTED POLYMER SENSORS	
5.1 Introduction	95
5.2 Development of Test Jig and Sensor Measurement System	95
5.2.1 Volatile Generating Bubbler System	96
5.2.1.1 Electrical Controller Unit	98
5.2.1.2 Sensor Cell and Characterization	99
5.2.2 QCM/IDE Measurement Setup	100
5.2.3 Figaro© 2620 Test setup	102
5.3 Results and Discussion	104
5.3.1 Selectivity Detection of MIP Sensor	104

5.3.2	Cross-Selectivity	106
5.3.3	Humidity Effect to MIP based Sensor	113
5.3.4	Sensitivity Detection of MIP Sensor	116
5.3.4.1	QCM-MIP Sensor Sensitivity	116
5.3.4.2	IDE-MIP Sensor Sensitivity	119
5.3.5	Comparison Analysis of IDE-MIP Sensor towards Figaro© Sensor	122
5.3.5.1	Discrimination of Different Concentrations using Figaro© 2620	123
5.3.5.2	Comparison of Sensor Repeatability Between Figaro© 2620 and MIP Sensor	126
5.3.5.3	Comparison of Response and Recovery Time for Figaro© 2620 and MIP Sensor	129
5.4	Summary	132

CHAPTER 6 TESTING OF MIP-BASED ARTIFICIAL OLFACTORY SENSOR SYSTEM FOR MANGO FRUIT MATURITY DETERMINATION

6.1	Introduction	134
6.2	Statistical Analysis	135
6.3	Real-time Monitoring of Volatile Emanations	135
6.4	ANOVA Analysis for Different Harumanis Mango Maturity Level	139
6.5	Overview of the Artificial Olfactory System	143
6.6	Artificial Olfactory System Operation	146
6.7	Summary	151

CHAPTER 7 CONCLUSIONS AND FUTURE WORKS

7.1	Conclusions	152
7.2	Future Work	155

REFERENCES	157
APPENDIX A	165
APPENDIX B	167
APPENDIX C	168
LIST OF PUBLICATIONS/ CONFERENCES	169
LIST OF AWARDS	172
OTHERS	173

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LIST OF FIGURES

NO.		PAGE
1.1	Production of Mango in Malaysia from 2006 to 2013 (National Mango Convention, 2013)	2
1.2	Thesis Methodology Summary	10
2.1	Comparison of Human Olfactory and Artificial Olfactory	15
2.2	Type of Common Sensing Principle Used for Chemical Gas Sensing	16
2.3	QCM Dimension	19
2.4	General Piezoelectric Oscillators	20
2.5	Molecular Imprint Polymer (MIP) Concepts	25
2.6	One-dimensional Grid Pattern IDC (Sontinuang et al. 2011)	29
2.7	Imprinting Efficiency of Microcontact-BSA Imprinted electrode vs. NIP electrode (Ertürk et al. 2014)	30
2.8	Frequency Shift when Exposed to Limonene Gas (14.35 ppm) of P- MIP and NIP sensor. (Kikuchi et. al. 2006)	31
2.9	QCM Sensor Response to Different Volatile Concentrations (Peter et al. 2009)	33
3.1	Schematic Diagram of GC process	38
3.2	Mass Spectrum is acquired using a variety of ionization	39
3.3	Schematic diagram of a typical GC-MS system diagram	40
3.4	Solid phase microextraction devices with holder	41
3.5	Schematic representation of SPME. a) First step represented by extraction/sampling; b.) Second step represented by desorption/injection	44
3.6	GC–MS experimental setup for mango volatile detection using (a) SPME (b) Headspace	45
3.7	GC–MS result on Harumanis mango (year 2012) with difference ripeness maturity week	48
3.8	GC–MS result on Harumanis mango (year 2013) with difference ripeness maturity week	49

3.9	PCA of the TIC chromatograms for Harumanis mango (batch 2013)	51
3.10	3D Scatter plot of TIC chromatograms for Harumanis mango (batch 2013)	52
3.11	PCA of the TIC chromatograms of Harumanis mango (batch 2012)	53
3.12	3D Scatter plot of TIC chromatograms for Harumanis mango (batch 2012)	53
3.13	Ripe Harumanis Mango Peak Area vs. Incubation time	54
3.14	GC–MS result on Sala mango with difference ripeness maturity week	55
3.15	TIC of RT 3.73 for (a) mature Sala mango (b) Near Ripe Sala mango	56
3.16	PCA Score for Sala mango	58
3.17	GC–MS result on Chukanan mango with difference ripeness maturity week	59
3.18	PCA score for Chukanan mango	60
3.19	A Gas chromatogram of α -pinene at different concentrations	62
3.20	Mass spectrum of α -pinene	63
3.21	Calibration curves at different concentration of (a) α -pinene, (b) terpinolene and (c) γ -terpinene from GC-MS	64
3.22	Comparison of Peak Area Count of with standard deviation error bars for ripe Harumanis flesh and skin	65
4.1	Principles of Molecular Imprinting	67
4.2	IDE Stainless Steel Main Mask Dimension	71
4.3	RF Sputtering System (Alfonso et al. 2006)	71
4.4	Flow for Molecular Modelling	73
4.5	Energy study between COOH group and template (Samsudin's thesis, 2013)	75
4.6	a) Imprinting process (polymerization) of α -pinene via hydrogen bonding. b) Removal of template molecule (α -pinene)	77

4.7	a) IDE sensor on PET substrates b) Schematic illustration of immobilization the MIP on PET substrates c) Removal of template molecule	78
4.8	Example of 8 possible attachment of 1 molecule MAA bind with a template, α -pinene (Samsudin's thesis, 2013)	80
4.9	Frequency shift (Δf) of MIP- γ -terpinene for different ratio analysis	83
4.10	Surface morphology of IDE using SEM with 0.5 mm electrode spacing (a) AU Electrode (b) PT Electrode	83
4.11	Surface morphology of IDE using SEM with 0.25 mm electrode spacing	84
4.12	Cross Section of an IDE-MIP Sensor	85
4.13	Comparison of SEM film morphology of (a) NIP (b) MIP	86
4.14	Comparison of AFM film morphology (a) NIP (b) MIP	86
4.15	EDX spectrum of whole slice IDE on PET	87
4.16	EDX element map for (a) gold (b) oxygen (c) carbon	88
4.17	Frequency shift of QCM MIP sensor with α -pinene as a template when exposed to α -pinene volatile	89
4.18	Capacitance shift of IDE-MIP Sensor responses with γ -terpinene as a template when exposed to γ -terpinene volatile	90
4.19	Capacitance value for different IDE dimensions	94
5.1	Schematic diagram of a sensor measurement system showing the volatile generating bubbler and sensor cell chamber	96
5.2	Sample fabricated Teflon chamber	100
5.3	A schematic diagram of the apparatus for QCM/IDE multi-sensor	101
5.4	Block diagram of the Figaro testing setup	102
5.5	Measuring circuit for TGS2620 sensor	103
5.6	Data Acquisition Interface	103
5.7	Frequency Shift of NIP and MIP after exposed to α -pinene gas (39.5ppm)	105

5.8	Capacitance Shift of NIP and MIP after exposed γ -terpinene gas (236.5 ppm)	106
5.9	Frequency shift of MIP multi-sensor after exposed to terpinolene gas (14.3 ppm)	107
5.10	Frequency shift of MIP multi-sensor after exposed to γ -terpinene gas (54.6ppm)	108
5.11	Frequency shift of MIP multi-sensor after exposed after exposed to α -pinene gas (37.7 ppm)	109
5.12	Capacitance shift of MIP multi-sensor after exposed to γ -terpinene gas (121.6ppm)	111
5.13	Selectivity pattern of MIP when exposed to terpinolene gas (14.3ppm)	112
5.14	Capacitance shift of an array of mip after exposed to α -pinene gas (60.7ppm)	113
5.15	The frequency shift of MIP and NIP sensors exposed to limonene gas(5.4 ppm), as a function of relative humidity	114
5.16	The capacitance shift of MIP and NIP sensors exposed to limonene gas (5.4 ppm), as a function of relative humidity	115
5.17	Detection of different QCM-MIP sensors at lower sensitivity concentration	117
5.18	Calibration curve of different QCM-MIP sensors	119
5.19	Detection of different IDE-MIP sensors at lower sensitivity concentration	120
5.20	Calibration curve of different QCM-MIP sensors	122
5.21	Figaro 2620 response when exposed to different ethanol concentration	124
5.22	Figaro 2620 response when exposed to different limonene and γ -terpinene concentration	125
5.23	Repeatability of Figaro 2620 and QCM-MIP sensor towards terpinolene volatiles (13.11 ppm)	127
5.24	Repeatability of Figaro 2620 and IDE-MIP sensor towards limonene volatiles (5.4 ppm)	128

5.25	Sensor response of Figaro 2620 and QCM-MIP sensors when exposed in the same time to γ -terpinene volatiles (102 ppm)	130
5.26	Typical Sensor Response	130
6.1	Monitoring of Volatiles from Ripe Harumanis Mango by IDE-MIP Sensors	136
6.2	Early Observation of Volatiles Emissions Profile Ripe Harumanis Mango by IDE-MIP sensors	138
6.3	Mature Harumanis ANOVA Analysis. Groups not connected by interval were found to be significantly different at $\alpha = 0.05$	140
6.4	Early Ripe Harumanis ANOVA Analysis. Groups not connected by interval were found to be significantly different at $\alpha = 0.05$	141
6.5	Ripe Harumanis ANOVA Analysis. Groups not connected by interval were found to be significantly different at $\alpha = 0.05$	141
6.6	Block diagram of the Olfactory system	144
6.7	Top view of the electronic circuit designed for multi sensor system	145
6.8	Top view of the pump casing box	145
6.9	Flow chart of the MIP Olfactory Testing Procedure	148
6.10	Calibration of each sensor to detect the baseline capacitance	149
6.11	Sensor to detect the capacitance change	149
6.12	Different Maturity Stage of the Olfactory system	150

LIST OF TABLES

NO.		PAGE
2.1	Analytical Characteristic of QCM-MIP based Sensor	27
2.2	Composition Ratio of MIP Solutions (Kikuchi et. al, 2006)	32
3.1	Description of Maturity Stages and Ripeness Level of Harumanis Mango	42
3.2	MS Profile for Injector temperature and Ionization Energy	46
3.3	Volatile Compounds Emitted from Mature, Nearly Ripe and Ripe Harumanis Mangoes	50
3.4	Volatile Compounds Emitted from Mature, Nearly Ripe and Ripe Sala Mangoes	57
3.5	Volatile Compounds Emitted from Mature, Nearly Ripe and Ripe Chukanan Mangoes	60
3.6	Comparison of α -Pinene, γ -terpinene and terpinolene for Harumanis, Sala and Chukanan Mango	66
4.1	Result of Energies Calculation (template α -pinene, γ -terpinene and terpinolene) for All Possible Ratios (Samsudin's thesis, 2013)	81
4.2	Optimum Composition Ratio (template: MAA :EGDMA)	83
5.1	Vapor Pressure Used by the System	98
5.2	Comparison of Figaro 2620 and MIP Sensor Response	132
6.1	ANOVA for Impacts of Mango Volatiles for Ripe Harumanis	142
6.2	Capacitance Shift Range for Harumanis Mango Volatiles Emission (60s)	147
6.3	Classification Results with Harumanis Samples	150

LIST OF ABBREVIATIONS

AET	Aminoethanethiol
AFM	Atomic Force Microscopy
AIBN	Azobisisobutyronitrile
ANOVA	Analysis of variance
APTS	Trimethoxysilane
BAW	Bulk Acoustic Wave
CAR/PDMS	Carboxen/poly(dimethylsiloxane)
CDC	Capacitance Digital Converter
CP	Conducting Polymer
CPU	Central Processing Units
CW/DVB	Carbowax/divinylbenzene
DAQ	Data Acquisition Card
DVB/CAR/PDMS	Divinylbenzene/Carboxen/poly(dimethylsiloxane)
EDX	Energy-dispersive X-ray Spectroscopy
EEPROM	Electrically Erasable Programmable Read-Only Memory
EGDMA	Ethylene Glycol Dimethacrylate
E-nose	Electronic noses
FETs	Field Effect Transistors
GC-MS	Gas Chromatography-Mass Spectrometry
GUI	Graphical User Interface
HMI	Human Machine Interface
I/O	Input/Output
I ² C	Inter Integrated Circuit
IDC	Interdigitated Capacitive

IDE	Interdigitated Electrode
LCD	Liquid Crystal Display
LSD	Least Significant Difference
m/z	Mass/Charge Ratio
MAAP	Methacryl-amidoantipyrine
MFC	Mass Flow Controllers
MIP	Molecularly Imprinted Polymer
MMA	Methacrylic Acid
MOS	Metal Oxide Semiconductor
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
MS	Mass Spectrometer
NIP	Non-Imprinted Polymer
NIST	National Institute of Standards and Technology
PA	Polyacrylate
Pani	Polyaniline
PCA	Principal Component Analysis
PCs	Principal Components
PET	Polyethylene Terephthalate
PLC	Programmable Logic Controller
PPM	Part Per Million
PPy	Polypyrrole
PTFE	Polytetrafluoroethylene
PTh	Polythiophene
QCM	Quartz Crystal Microbalance
QMB	Quartz Microbalance
RAM	Read Access Memory

R ₀	Figaro 2620 Sensor resistance in 300ppm of ethanol
R _s	Figaro 2620 Sensor resistance in displayed gases at various concentrations
RSD	Relative Standard Deviation
RT	Retention time
SAW	Surface Acoustic Wave
SCCM	Standard Cubic Centimeters per Minute
SCL	Serial Clock Line
SDA	Serial Data Line
SIFI	Selected Ion Full Ion
SIR	Single Ion Recording
SPI	Serial Peripheral Interface
SPME	Solid Phase Micro Extraction
SPR	Surface Plasmon Resonance
TEOS	Tetraethoxy-silane
THF	Tetrahydrofuran
TIC	Total Ion Chromatograph
TSM	Thickness-Shear Mode
TSS	Total Soluble Sugars
UART	Universal Asynchronous Receiver Transmitter
UV	Ultra Violet
VOC	Volatile Organic Compounds
ΔC	Capacitance Change
ΔHz.	Frequency Change
ΔE	Energy Difference

Sensor Molekul Bercetak Polimer (MIP) Yang Sangat Selektif Untuk Menentukan Kematangan Buah

ABSTRAK

Kematangan buah boleh ditentukan dengan menggunakan alat olfaktometri buatan seperti sistem hidung elektronik. Walaubagaimanapun, prestasi sistem hidung elektronik terhad disebabkan beberapa isu pada kebolehan gas sensor yang sedia ada seperti tahap selektif yang rendah dan memerlukan suhu operasi yang tinggi. Salah satu alternatif penyelesaian kepada kekurangan gas sensor yang digunakan oleh hidung elektronik ialah dengan menggunakan sensor molekul bercetak polimer. Tesis ini akan membincangkan tentang pembangunan sensor polimer molekul bercetak (MIP) yang sangat selektif dan mampu untuk mengikat dengan ruapan mangga. Penentuan kematangan buah-buahan sentiasa menjadi aspek yang sangat penting dalam bidang pertanian terutamanya dalam pengredan kualiti buah-buahan. Melalui kajian kromatografi gas jisim spektrofotometer (GCMS), zat ruapan mangga (α -pinene, terpinolene dan γ -terpinene) telah berjaya dikenal pasti sebagai penanda kematangan. Kematangan buah mangga yang berbeza juga telah didapati akan mengeluarkan corak ruapan yang tertentu. Dari perisian pemodelan Hyperchem, nisbah optimum MIP (templat: MAA:EDGMA) untuk α -Pinene dan γ -terpinene didapati adalah 1: 5: 20, manakala bagi terpinolene, nisbah optimumnya ialah 1: 3: 20. Dengan menggunakan maklumat penanda kimia ini, sensor MIP akan dibangunkan untuk setiap ruapan mangga yang dipilih dan diintegrasikan bersama elektrod interdigit (IDE) dan Kuarza Kristal Timbangan (QCM) sebagai transduser. Sensor MIP adalah sangat selektif dalam membezakan zat meruap termasuk isomer. Tambahan pula, sensor MIP juga adalah sangat sensitif untuk mengesan penanda kimia kepekatan dengan serendah 1.7 ppm. Berbanding dengan sensor oksida logam semikonduktor (MOS), sensor MIP juga telah menunjukkan respons/pemulihan dan kebolehulangan sensor yang sangat baik daripada sensor MOS. Sensor MIP juga telah didedahkan dengan pelbagai sampel buah mangga serta buah mangga yang berbeza peringkat kematangan dan telah berjaya bertindak balas terhadap ruapan sasarannya. Sistem MIP sensor juga kemudian telah dibangunkan bagi memantau secara nyata pelepasan ruapan mangga dan telah juga berjaya menentukan kematangan buah mangga Harumanis dengan keputusan yang baik. Dalam kajian ini, pendekatan menggunakan MIP sebagai satu elemen pengesanan samada sebagai sensor atau sistem deria telah berjaya dibangunkan. Oleh kerana sistem MIP ini adalah sangat selektif, ianya boleh dibangunkan dengan kos yang minimum dengan harapan menjadi suatu kaedah alternatif dalam menentukan kematangan buah tanpa memusnahkan sampel buah-buahan yang diuji. Bagi petani, ini mampu meningkatkan pemahaman mereka tentang kematangan buah dan seterusnya akan menyumbang kepada peningkatan pengeluaran kualiti buah.

HIGHLY SELECTIVE MOLECULARLY IMPRINTED POLYMER (MIP) BASED SENSOR FOR FRUIT MATURITY DETERMINATION

ABSTRACT

Fruit maturity can be determined by using artificial olfactory equipment such as electronic nose system. However, the electronic nose system performance is limited due to several issues on existing gas sensor capability such as low selectivity and high temperature operation. An alternative is to use molecularly imprinted polymers (MIP) based sensors. This thesis discussed about the development of MIP sensors that are highly selective and able to bind with mango volatiles. Detection fruit maturity level has always been a very important aspect of final fruit quality grading in agriculture. From gas chromatography mass spectrophotometer (GCMS) studies, mango volatiles (α -pinene, terpinolene and γ -terpinene) were identified as maturity marker. It was found mangoes different maturity level will emit specific maturity marker pattern. By using Hyperchem Modelling, MIP optimum ratio (template: MAA:EDGMA) for α -pinene and γ -terpinene were found to be at 1:5:20, while for terpinolene, the MIP optimum ratio was 1:3:20. Utilizing this information, the MIP sensor was first developed per the selected maturity marker. It was then integrated with Interdigitated Electrode (IDE) and Quartz Crystal Microbalance (QCM) as transducer. MIP sensor was highly selective in discriminating any non-target volatiles including isomers. Furthermore, the MIP sensor was highly sensitive to detect chemical marker as low as 1.7 ppm concentration. When compared to a metal oxide semiconductor (MOS) sensor, it was observed that the MIP sensor also offers excellent sensor response/recovery and repeatability than the MOS sensor. The MIP sensor was also exposed real time to mango with different maturity stages where the sensor response pattern responded towards its target analyte at various maturity phases. A multi sensor based MIP system was also developed to provide real-time monitoring of mango volatiles emission and has successfully determined Harumanis mango maturity with good scores. Since the MIP olfactory system is highly selective, low power and can be developed with minimum cost, this can be an alternative to provide an effective and non-destructive method for fruit maturity determination. For farmers, improving their understanding about the fruit maturity would certainly contribute to an increase of fruit production and quality.

CHAPTER 1

INTRODUCTION

1.1 Introduction

One of the most important technological aspects in the agriculture industry is determining fruit maturity and its time to harvest. This is important because the fruits that are harvested has important effects on the consumer satisfaction level. Having the situation of not knowing when the fruit has reached their preferred state of ripeness can be frustrating for consumers. At the end, this can create some barrier for consumers to purchase. The fruits harvested either in over ripe or unripe, would have a major effect on the shelf life. If the fruit is harvested over ripe, then it would likely to become soft quickly, wrinkled and shorter shelf life. On the other hand, if the harvest was going through an immature process, the fruits will tend to be in an unfavorable taste and lack of flavor. Moreover, valuable nutritions such as vitamins will tend to degrade and hence downgrading the overall fruits quality. For premium fruits that are intended for international market, this could be financially damageable as lower consumer satisfaction would eventually led to lower sales and profit.

The term mature describes the stage at harvest that will ensure that the fruit's quality will meet or exceed the minimum level which is acceptable to the consumer at the time it is consumed (Reid, 2002). During harvest, identifying the maturity level is critical to the development of good flavor quality in the fruit when fully ripe (Kader, 2008). Thus, it is important to have effective methods of determining fruit maturity. For most fruits, this

could be challenging as the inner and outer properties of the fruit would still continue to change even after harvesting.

Mango (*Mangifera indica* L.) is one of the most popular fruit of the tropics. It is reported that there have been an increase of worldwide mango import demand of 97,623 metric tons in 1996 to 826,584 metric tons in 2005 (Evans, 2008). Growing worldwide interest in mango has also been due to the increased knowledge of the health benefits derived from mango consumption. Apart from having high levels of vitamin C and fibers, mangoes are known to have certain antioxidants, which are believed to be helpful against colon, breast, leukemia and prostate cancers. In Malaysia, the mango industry has grown remarkably over the past years (Figure 1.1).

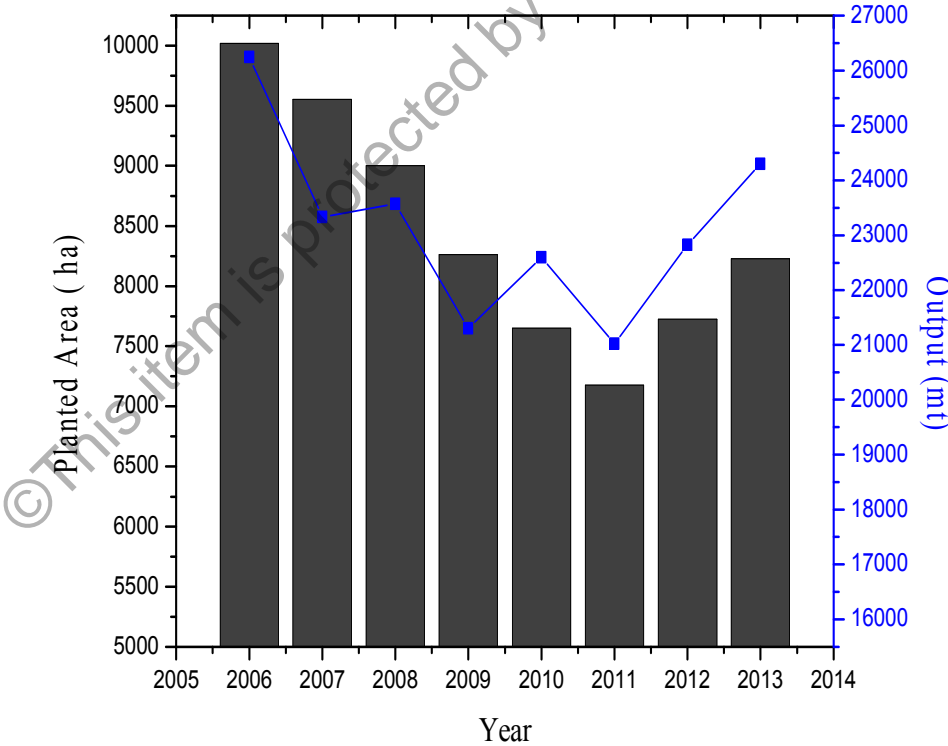


Figure 1.1 Production of Mango in Malaysia from 2006 to 2013 (National Mango Convention, 2013)

In Perlis for example, it played an important role in revitalizing the rural economy. In the third National Agricultural policy (NAP3), mango was identified as among 15 types of fruit to be developed as an export crop. Harumanis deemed as the 'king of mangoes' and also known as seasonal fruit that can only be available from April to May. Since the production is only available for short period of time, this has transformed Harumanis as a rare delicacy with premium price. The price of Harumanis can go up to RM35 per kilo, but this has not stopped people from buying boxes of this succulent, tropical fruit. According to Harian Metro news on 5 May 2015, 3,200 metric tons of Harumanis are expected to be harvested in 2015, in comparison to just 500 metric tons only in 2012.

Harvesting mango has always been a delicate task as this type of fruit will continue to ripe even after harvested. It is important to harvest the crop in the right maturity stage and make it available to the market in the best possible condition. As such, there is a need to find an effective, objective and non-destructive method for the evaluation and prediction of the quality attributes of mangoes during maturation. This will certainly help the farmers to improve their understanding about the fruit maturity as well as to increase the fruit production.

1.2 Maturity Determination

Improving the selection of fruit maturity has always been a subject of interest for farmers, vendors and even consumers. As fruit production increased tremendously in the past decades, there has always been continuous demand to improve the conventional method. This is important as the conventional method is usually destructive and labor intensive. Furthermore, everyone may have different perception about the ideal ripeness of