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

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My parents, my wife, kids and newborn baby.
This is for you.

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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^2C	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_o	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 penggredan 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 menunjukan 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).

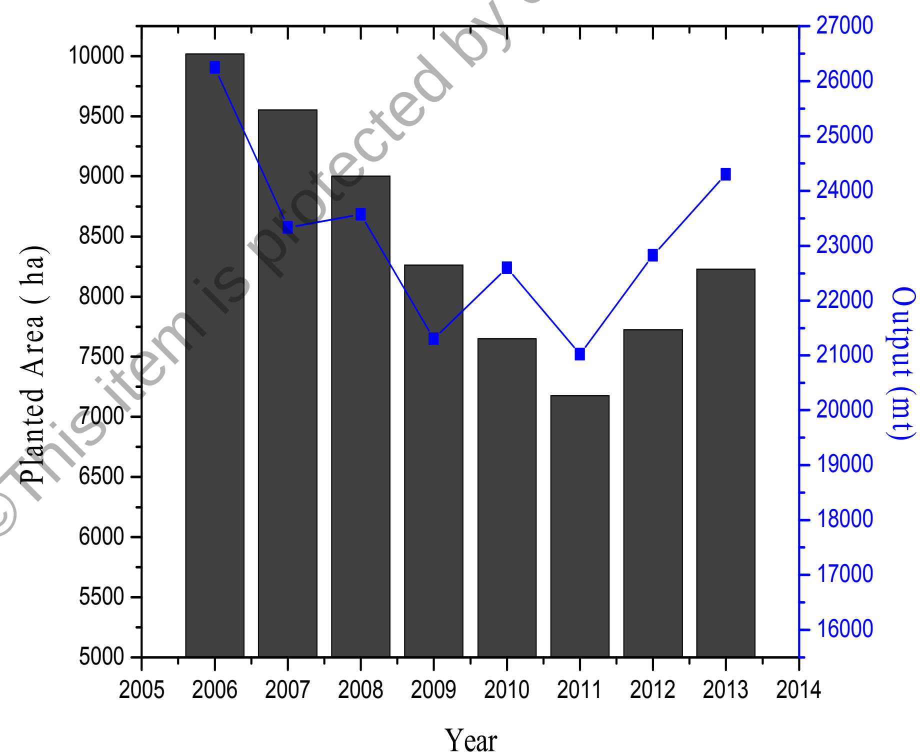

Figure 1.1 Production of Mango in Malaysia from 2006 to 2013
(National Mango Convention, 2013)