



***DYNAMIC MATHEMATICAL MODELLING OF FREE FATTY ACID
ACCUMULATION IN FRESH OIL PALM FRUIT (*Elaeis guineensis* Jacq.)***

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By

SHEHU UMAR ETSU

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree Doctor of Philosophy**

November 2019

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DEDICATION

I dedicate this thesis to my beloved wife in person of Hajiya Hadiza Yunusa Umar, and my children Khadijat Anisa Umar, Abubakar Sadeeq Umar, Muhammad Al-Amin Umar and Zainab Sakinat Umar for their unwavering love, sacrifice, patience, encouragement and best wishes.



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

DYNAMIC MATHEMATICAL MODELLING OF FREE FATTY ACID ACCUMULATION IN FRESH OIL PALM FRUIT (*Elaeis guineensis* Jacq.)

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November 2019

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Faculty : Engineering

Crude palm oil (CPO) is extracted from the fleshy mesocarp of the oil palm fruits, (*Elaeis guineensis*). The fruit has to undergo several thermo-mechanical processes before the oil can be extracted. However, the oil-bearing mesocarp of the fruit contained an endogenous enzyme (lipase), which is activated upon injury/bruised. The hydrolytic activity of the enzyme leads to the accumulation of free fatty acid (FFA) which is a major quality index of CPO. Researches have shown that over 2% of fresh fruit bunches (FFB) arriving at the mill are bruised and the bulkiness coupled with the close-knitted nature of the FFB causes ineffective heat distribution/penetration into the inner layers of the fruits during the steam sterilization process, which is aimed in inactivation of the enzyme. Hence, the need to explore alternative medium of heat transfer. Heating of the extracted CPO with high moisture content to facilitate handling in the mill triggered up thermal hydrolysis at a temperature above 100°C (373 K). All these phenomena simultaneously led to poor palm oil quality. Therefore, a method for the quantification of a bruise was developed and used for this study. Bruise volume, storage temperature and time were found to have a significant effect ($P < 0.05$) on FFA accumulation in oil palm fruits. Dynamic simulation of FFA in bruised fruits was used to predict the optimum temperature for FFA accumulation in bruised fruit to be 31°C (304 K). The GC-MS analysis of extracted CPO from bruised fruit heat-treated in chlorinated water indicates the formation of chlorinated fatty acids (Palmitic acid chloride and Lauric acid chloride). A wounding assay of the endogenous lipase in palm fruit was carried out to quantify in-vivo activity of the enzyme and the FFA accumulation in the fruitlets. A time-dependent heat penetration simulation was also conducted using a COMSOL Multiphysics software along with the development of kinetic models for thermal inactivation of lipase and thermal hydrolysis of CPO. The model equations were solved and the parameters of the model estimated using gPROMS ModelBuilder. The two-way analysis of variance (ANOVA) shows that treatment duration and temperature had significant ($P < 0.05$) effect on the residual lipase activity. The inactivation kinetics of lipase was found to

be a non-elementary reaction in which initial rate constant, k_{0dec} and inactivation energy, E_{dec} were estimated to be $0.035 \text{ U}^{-0.85}/\text{kg-mes}^{-0.85}\cdot\text{min}$ and 153052 kJ/kmol , respectively. The predicted residual activity fitted very well to the experimental data with relative root mean square error (rRMSE) between 0.19% and 1.17%. The important parameters for the thermal hydrolysis model estimated were activation energy, E (57554 kJ/kmol) and a frequency factor of reaction, k_0T ($2.14 \times 10^{-6} \text{ m}^3/\text{kmol}\cdot\text{min}$). The relative root means square error (rRMSE) between the measured and the predicted FFA accumulation is between 1.92% and 31.98%. This indicates a satisfactory fit between the experimental and the predicted values. The sensitivity analysis of the developed models (bruise, thermal inactivation of lipase and thermal hydrolysis) revealed that they are sensitive to the selected parameters k_{cat} , n_b , k_{0dec} , n_d , n_w , n_T and n . These kinetic models provided a basic understanding of the mechanism of FFA accumulation in palm fruits and CPO during handling and processing and may be a useful tool in further re-designing and quality improvement of the industrial processes of crude palm oil extraction. However, to mitigate against associated problems of the current steam sterilization, hot water sterilization should be explored.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

KAJIAN TERHADAP AKTIVITI PENGUMPULAN ACID LEMAK BEBAS (FFA) BUAH KELAPA SAWIT MENTAH

Oleh

SHEHU UMAR ETSU

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Minyak sawit mentah (CPO) diekstrak daripada mesokarpa buah kelapa sawit, (*Elaeis guineensis*). Buah ini perlu menjalani beberapa proses termal-mekanikal sebelum minyak dapat diekstrak. Walaubagaimanapun, mesocarp yang mengandungi minyak mempunyai enzim endogen (lipase), yang diaktifkan apabila diasingkan atau ketika buahnya lebam. Aktiviti hidrolisis enzim yang membawa kepada pengumpulan asid lemak bebas (FFA) yang merupakan indeks kualiti utama CPO. Penyelidikan telah menunjukkan bahawa lebih daripada 2% buah tandan segar (FFB) yang tiba di kilang telah lebam dan sebahagian besarnya digabungkan menyebabkan penyebaran haba / penembusan haba yang tidak berkesan ke lapisan dalam buah semasa proses pensterilan wap yang bertujuan untuk penyah-aktifan enzim. Untuk itu, terdapat keperluan untuk mengkaji medium alternative penyebaran haba. Semasa pemanasan CPO yang diekstrak dengan kandungan kelembapan yang tinggi untuk memudahkan pengendalian dalam kilang mencetuskan hidrolisis haba. Semua fenomena ini merendahkan kualiti minyak sawit. Kajian terbaru mengenai kualiti CPO dari kilang hanya memberi tumpuan kepada pengoptimuman parameter dan korelasi atau regresi dengan sedikit perhatian terhadap mekanisme pengumpulan FFA. Oleh kerana itu, ini menjadi keperluan untuk mengkaji kinetik pengumpulan FFA dalam CPO. Kaedah untuk mengukur lebam telah dibangunkan dan digunakan. Isipadu / kandungan lebam, suhu dan masa penyimpanan didapati mempunyai kesan yang ketara ($P < 0.05$) terhadap pengumpulan FFA dalam buah kelapa sawit. Satu simulasi dinamik FFA dalam buah lebam digunakan untuk meramalkan suhu optimum untuk pengumpulan FFA dalam buah lebam adalah $31\text{ }^{\circ}\text{C}$ (304 K). Analisis GC-MS CPO yang diekstrak dari haba buah lebam yang dirawat dalam air berklorin menunjukkan asid lemak monochloro-propanediol (MCPD). Ujian yang mencederakan lipase endogen dalam buah sawit dilakukan untuk mengukur aktiviti enzim in-vivo dan pengumpulan FFA dalam buah. Simulasi penembusan haba yang berkadar langsung dengan masa juga dijalankan menggunakan perisian COMSOL Multiphysics bersama-sama dengan pembangunan model kinetik untuk penyah-aktifan lipase dan hidrolisis haba CPO. Persamaan model telah diselesaikan dan parameter penting telah dianggarkan menggunakan perisian ModelBuilder gPROMS. Analisis dua hala (ANOVA)

menunjukkan bahawa tempoh rawatan dan suhu mempunyai kesan yang signifikan ($P < 0.05$) terhadap sisa aktiviti lipase. Kinetik *lipase* yang tidak aktif didapati sebagai tindak balas bukan asas di mana kadar permulaan, k_{0dec} dan tenaga tidak aktif, E_{dec} dianggarkan berjumlah $0.035 \text{ U}^{-0.85} / \text{kg-mes}^{-0.85} \cdot \text{min}$ dan $153052 \text{ kJ} / \text{kmol}$. Kajian ini juga mendedahkan bahawa tidak terdapat pengumpulan FFA yang ketara disebabkan hidrolisis termal dalam suhu kajian $35 \text{ }^\circ\text{C}$ (308 K) - $70 \text{ }^\circ\text{C}$ (343 K). Sisa aktiviti yang diramalkan dan pengumpulan FFA berpadanan dengan sangat baik dengan data eksperimen dengan ralat min (rRMSE) antara 0.19% dan 1.173%. Parameter penting untuk model hidrolisis terma yang dianggarkan adalah tenaga pengaktifan, E ($57554 \text{ kJ} / \text{kmol}$) dan faktor tindak balas frekuensi, k_{0T} ($2.14 \times 10^{-6} \text{ m}^3 / \text{kmol} \cdot \text{min}$). Ralat (rRMSE) antara pengukuran dan pengumpulan FFA yang diramalkan adalah antara 1.92% dan 31.98. Ini menunjukkan kesesuaian antara percubaan dan nilai yang diramalkan. Analisis sensitiviti model (kelembaman, suhu lipase tidak aktif, dan hidrolisis termal) menunjukkan bahawa mereka sensitif terhadap parameter k_{cat} , n_b , k_{0dec} , n_d , n_w , n_T dan n . yang dipilih. Model kinetik yang dibangunkan memberikan pemahaman kepada asas mekanisme pengumpulan FFA dalam buah sawit dan CPO semasa aktiviti pasca-tuaian dan boleh menjadi alat yang berguna dalam mereka bentuk semula dan meningkatkan kualiti proses perindustrian pengekstrakan minyak sawit. Walaubagaimanapun, untuk mengurangkan permasalahan berkaitan pensterilan wap pada masa kini, pensterilan menggunakan air panas perlu dikaji.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS AND NOMECLATURE

FFB	Fresh fruit bunch
OPF	Oil palm fruit
TAG	Triacylglyceride
MAG	Monoglycerides
DAG	Diglycerides
FFA	Free fatty acid

Nomenclature

Symbol	Unit	Description
A	$\text{m}^3/\text{kmol}\cdot\text{min}$	Arrhenius constant
A_g	m^2	Area of heater wall-gas phase
A_h	m^2	Exposure area of heater to outside
A_l	m^2	Area of heater wall-liquid phase
A_{wv}	m^2	Surface area of liquid phase
B_T	K	Constant for ratio constant evaporation to condensation
c_i	kmole/m^3	Molar concentration of component i
C_{Pair}	$\text{kJ}/\text{kg}\cdot\text{K}$	Specific heat capacity of dry air
C_{Ph}	$\text{kJ}/\text{kg}\cdot\text{K}$	Specific heat capacity of heater
C_{Pi}	$\text{kJ}/\text{kg}\cdot\text{K}$	Specific heat capacity of component i
C_{Pv}	$\text{kJ}/\text{kg}\cdot\text{K}$	Specific heat capacity of vapor
c_E	$\text{U}/\text{kg}\cdot\text{mes}$	Lipase activity
c_{mi}	$\text{kmol}/\text{kg}\cdot\text{mes}$	Molar concentration of component i
C_{pm}	$\text{kJ}/\text{kg}\cdot\text{K}$	Specific heat capacity of mesocarp
C_{ps}	$\text{kJ}/\text{kg}\cdot\text{K}$	Specific heat capacity of shell
C_{pk}	$\text{kJ}/\text{kg}\cdot\text{K}$	Specific heat capacity of kernel
E	kJ/kmol	Activation energy of reaction
E_{dec}	kJ/kmol	Deactivation energy
f	Dimensionless	Ratio of evaporation to condensation coefficient
fa	min.	Constant
f_i	$\text{kg}/\text{kg}\cdot\text{mes}$	Mass fraction of component i
$f_{oil\ cell}$	$\text{kg}/\text{kg}\cdot\text{mes}$	Mass fraction of oil
f_{i0}	$\text{kg}/\text{kg}\cdot\text{mes}$	Mass fraction of oil
f_T	-	Temperature correlation
H_{eva}	kJ/kg	Enthalpy of evaporation

h	$\text{kJ/m}^2 \cdot \text{K} \cdot \text{min}$	Convective heat transfer coefficients
h_{hg}	$\text{kJ/K} \cdot \text{m}^2 \cdot \text{min}$	Heat transfer coefficient of heater-gas phase
h_{hl}	$\text{kJ/K} \cdot \text{m}^2 \cdot \text{min}$	Heat transfer coefficient of heater-liquid phase
K	$\text{kJ/m} \cdot \text{K} \cdot \text{min}$	Thermal conductivity
k_{OT}	$\text{m}^3/\text{kmol} \cdot \text{min}$	Frequency factor of reaction
K_D	kJ/K	Derivative term constant
K_I	$\text{kJ/K} \cdot \text{min}^2$	Integral term constant
K_P	$\text{kJ/K} \cdot \text{min}$	Proportional term constant
K_{li}	$\text{kmol/kg} \cdot \text{mes}$	Concentration
k_{cat}	$\text{kg} \cdot \text{mes}/\text{U} \cdot \text{min}$	Catalytic constant
k_T	$\text{m}^3/\text{kmol} \cdot \text{min}$	Rate constant
k_{dec}	$\text{U}^{-0.85}/\text{kg} \cdot \text{mes}^{-0.85} \cdot \text{min}$	Inactivation rate
k_{0dec}	$\text{U}^{-0.85}/\text{kg} \cdot \text{mes}^{-0.85} \cdot \text{min}$	Initial inactivation rate
m	kg	Mass
m_{air}	kg	Mass of dry air
M_H	kg	Mass of heater
m_i	kg	Mass of component i
m_{i0}	kg	Initial mass of component i
M_m	kg	Mass of mesocarp
m_v	kg	Mass of vapour
MW_i	kg/kmol	Molecular weight of component i
N	-	Number of measured data
n_T	Dimensionless	Power factor for temperature relation
n	-	Power factor for water fraction
n_w	Dimensionless	Reaction order
n_d	Dimensionless	Reaction order
n_b	Dimensionless	Power constant of bruise
O_j		value of predicted data j
P_{air}	kPa	dry air pressure
P_{atm}	kPa	atmospheric pressure
P_t	kPa	total pressure
P_v	kPa	vapor pressure
P_{vs}	kPa	saturated vapor pressure
\dot{P}_{el}	kJ/min	electrical power
P_j	-	value of measured data j
\bar{P}_j	-	average value of measured data j
Q_g	kJ	energy in gas phase
Q_h	kJ	energy of heater
Q_l	kJ	energy in liquid phase
\dot{Q}_{loss}	kJ/min	heat transfer rate due to loss
\dot{Q}_{lv}	kJ/min	heat transfer rate due to evaporation

\dot{Q}_{hg}	kJ/min	heat transfer rate from heater to gas phase
\dot{Q}_{hl}	kJ/min	heat transfer rate from heater to liquid phase
RA	%	Relative activity
R_m	m	Radius of fruit
R_s	m	Radius of shell
R_k	m	Radius of kernel
R_s	kJ/kmol·K	Gas constant
R_a	Dimensionless	Ratio of bruise volume to mesocarp volume of fruit
rel_{act}	%	Relative activity
r_{hydepo}	kmol/m ³ ·min	reaction rate of hydrolysis of CPO
r_{hydmes}	kg/kg-mes·min	Reaction rate of hydrolysis CPO in the mesocarp
T	K	temperature in liquid phase
T_0	K	initial temperature in liquid phase
T_{amb}	K	ambient temperature
T_g	K	temperature in gas phase
T_h	K	temperature of heater
T_{set}	K	set temperature
T_w	K	Temperature of water
T_{opt}	K	Optimum temperature
T_{max}	K	Maximum temperature
T_{min}	K	Minimum temperature
U_h	kJ/K·m ² ·min	overall heat transfer coefficient
V	m ³	vessel volume
V_{maxT}	1/min	Reaction rate constant of reaction
V_{max0T}	1/min	Initial reaction rate constant of reaction
V_{max0T}	1/min	Initial reaction rate constant of reaction
V_g	m ³	gas phase volume
V_{g0}	m ³	initial gas phase volume
V_i	m ³	volume of component i
V_l	m ³	volume of liquid
V_{i0}	m ³	initial volume of component

V_{pe}	Dimensionless	Oil fraction
\dot{W}_{wv}	kg/min·m ²	specific water mass flow rate
X_{wat}	kg/kg	mass fraction of water

Subscripts

i	number of component
j	number of data
k	kernel
m	mesocarp
s	shall
w	water
a	air

Greek letters

Symbol	Unit	Description
η_{eva}	-	mass evaporation coefficient
ρ_i	kg/m	density of component i
η_{con}	-	mass condensation coefficient
α	m ² /min	thermal diffusivity

CHAPTER 1

INTRODUCTION

1.1 Overview of the Chapter

This chapter describes the background of the study on postharvest activities of oil palm fruit, its composition, increasing demand and concern for quality sustainability. Quality parameters, unit operations and practices during the extraction of crude palm oil (CPO) that contribute to oil degradation as results of free fatty acid (FFA) accumulation along the process line are highlighted. The problems associated with the current methods of fruits handling and processing, the objectives set to be achieved and the scope of work are also presented.

1.2 Background of the Study

Oil palm fruit (OPF) is a drupe fruit from palm tree (*Elaeis guineensis*). It is reddish in colour and grows in bunches. Each fruit is made up of an oily, fleshy outer layer (the mesocarp), with a single seed (the palm kernel). The oil extracted from the fruit mesocarp is known as crude palm oil (CPO) and the one from its kernel is called palm kernel oil. It is among the most economically important plant source for edible and industrial oil. According to European Palm Oil Alliance (EPOA, 2016), “the global palm oil production has increased from 15.2 million tons in 1995 to 62.6 million tons in 2015. This is the highest production volume of all vegetable oils, exceeding the second biggest oilseed crop by more than 10 million tons”. The main reasons behind this growth could be attributed to the high productivity nature of OPF, the discovery and development of new applications beyond the traditional food use such as production of biodiesel.

However, Malaysian Palm Oil Council (MPOC, 2018) reported that the global palm oil production for 2018 was projected at 70 million tonnes with Malaysia and Indonesia as leading producers. Malaysian palm oil production is projected to reach 20.3 million tonnes, in 2018 due to better yields. In addition, “the global consumption of palm oil which rose from 14.6 million tons in 1995 to 61.1 million tons in 2015 is estimated by World Bank to double by 2020 making it as the most consumed oil in the world” (EPOA, 2016).

Red palm oil is distinctive among vegetable oils because of its fatty acid (FA) and TAG composition. It also contains some minor components such as free fatty acids (FFA), monoacylglycerols (MAG), diacylglycerols (DAG), metals, phospholipids, peroxides, chlorophylls, carotenoids, phenolic compounds, and tocopherols (Lin, 2011). The mesocarp of the oil palm fruit also contains an endogenous enzyme (lipase), which is at a dormant state in an intact fruit but activated when the fruit is bruised (Ngando-Ebongue *et al.*, 2006).

The bruising of the fruits caused mixture of the TAG and the cytoplasm fluid (water) to mix up forming an emulsion within the damaged area. TAG- water mixture is a favourable interface for hydrolytic activity of the endogenous lipase. The opening created by the bruised action also makes the fruits to be prone to invasion by microorganisms. The combined hydrolytic activities of both endogenous and microbial lipases inside the fruits before the commencement of any milling activity leads to FFA accumulation in the un-processed fruits.

At the time of harvest, the level of FFA in ripe, unbruised fruit is between 0.2% to 0.7% (Wahyu *et al.*, 2016) but in-appropriate handling can cause the FFA to rise rapidly. FFA contents increment to about 40% in 15 minutes after mesocarp damage has been reported by Pahoja and Sethar (2002) and Ngando-Ebongue *et al.* (2006). Between the period of harvesting and processing of FFB at the mill, the bunches are also subjected to a series of handling and transportation methods in which they are exposed to physical/mechanical damage often referred to as bruise. The damage is due to the falls of the fruit bunch from the tree during harvesting, machinery and mishandling during transportation.

Research has shown that about 2.88% of harvested FFBS are bruised (Hadi *et al.*, 2009). This certainly will contribute to the amount of FFA that will accumulate in the fruits before the fruits reach the mill reception ramp. The rate of increase in FFA of the fruit is directly proportional to the severity of bruise to the fruits (Xern, 2017), which is a function of the amount and method of transportation and handling of the bunches. The increase in FFA is also dependent on the time elapsed between harvesting and sterilization.

According to Abdull Rani *et al.* (2015), the quality of CPO is commonly measured by five parameters, i.e. FFA content, the deterioration of bleachability (DOBI), iodine value, moisture content and carotene content. However, Constant *et al.* (2017) reported that the quality of palm oil is assessed mainly by its FFA content and impurities. The accumulation of FFA has a strong impact on the quality of CPO because FFA content above 5% is thought to be unfit for human consumption (Ngando-Ebongue *et al.*, 2006). Hence, FFA content can be said to be the most cardinal parameter in the quality assessment of CPO as it influences consumer decision and trading of the commodity.

The first step towards curtailing FFA accumulation in CPO is to minimise mechanical damage/bruise to the mesocarp and to carryout effective heat treatment to inactivate the endogenous lipase. However, heat treatment of FFB to inactivate the endogenous lipase is indispensable but care must be taken to deliver adequate heat needed to inactivate the enzyme. Apart from the enzymatic reactions that may take place during sterilization, Noerhidajat *et al.* (2016) reported that the possibility of hydrolysis during sterilization is high since most of the oil-bearing cells are plant tissue with water content. Jusoh *et al.* (2013) also reported the influence of heating parameters of the milling process on the quality of CPO. They recommended a precise study for the improvement of CPO quality with special attention to the FFB sterilization

process.

It is therefore, pertinent to understand the interactions between the parameters of postharvest activity, their effects and the mechanisms of FFA accumulation in the extracted CPO. The ideal approach to achieve this understanding, is to model the kinetics of the reactions that occurred in the fruits before, during and after milling. Such models are currently very scarce hence, the need for this study.

1.3 Problem Statements

Oil palm fruit (OPF) is subjected to several mechanical and thermal processes before CPO can be extracted from it. The nature of palm fruit tree, the current method of harvesting and handling of FFB causes a lot of mechanical damage to the thin, pliable exocarp of the fruit. The damage to the mesocarp ruptures the oil-bearing cells, mixing the oil with the cytoplasm fluid (water) to form an emulsion which is a good interface for enzymatic hydrolysis leading to the accumulation of FFA.

The storage/delay time of the injured/bruise OPF is also a major problem that could activate the lipase and instantly brings about accumulation of FFA. The damage to the exocarp makes the fruit to be prone to invasion by microorganisms which also hydrolyses the oil (triglycerides) with their lipase. The product of the hydrolysis (FFA) affects CPO quality in terms of wholesomeness and commercial value. This was attested to by Ngando-Ebongue *et al.* (2006) and Kumar & Krishna (2014) who reported that high FFA CPO is unfit for human consumption and may lead to a loss of 13.6 to 19.5% neutral lipid during refining respectively.

Apart from the above, higher FFA in CPO implies higher DAG, MAG and glycerol which has been reported by Taylor *et al.* (2013) to be precursor for the formation of fatty acid esters of monochloro-propanediol (MCPD) and that of glycidol. Glycidol and 3-MCPD pose concerns for food safety. Reports of toxicological studies have shown that “free 3-MCPD is carcinogenic in rats, producing kidney and reproductive system defects” (MacMahon *et al.*, 2013). This therefore, necessitated the Joint Food and Agriculture Organization/ World Health Organization Expert Committee on Food Additives (JECFA) to recommend a maximum tolerable daily intake for free 3-MCPD to be 2 µg/kg body weight per day (MacMahon *et al.*, 2013)

The sterilization process carried out at 131°C (404 K) and 40 psi, to ease the detachment of fruitlets from spikelet and also to inactivate the lipase is also face with the problem of the close-knitted arrangement of spikelet. This, in addition to the whole loading of FFB during sterilization prevents heat to effectively penetrate through the fruits or evenly distribute within the bunch as well as within the cage. Thereby resulting in ineffective sterilization of the fruits to be responsible for low oil recovery and the quality of the extracted CPO (Ali *et al.*, 2014). The ineffectiveness of the sterilization process could lead to the differential cooking of the fruits and consequently resulting to partial inactivation of the endogenous lipase in the fruits.

The uneven distribution of steam also causes certain parts of FFB to be overcooked leading to gradual accumulation of FFA due to thermal-induced chemical hydrolysis. Determination of the effectiveness of sterilization in-situ is practically difficult since the process cannot be empirically observed directly, the current process practiced in palm oil mills according to Yunus *et al.* (2015) is not well understood.

According to Sarah and Taib (2013), several studies on palm fruit sterilization has been published but only a few of them reported on the enzymatic destruction kinetics of lipase during sterilization of oil palm fruits. The different physical parameters such as temperature, pressure, heating time used during processing of FFB for CPO and water content of the oil will cause changes in physical and chemical properties of the CPO. During milling, thermal hydrolysis of the TAG due to high temperature (>100°C) and moisture is prevalent. Extreme heat, moisture content and extended heating hour initiate hydrolysis of the CPO to the point that the reaction becomes dominant. Manral *et al.* (2008) reported that “repeated heating of CPO at high temperatures results in thermal degradation reactions leading to changes in its physical, chemical, nutritional and sensory properties”, thereby, reducing the quality of CPO produced.

Deterioration and degradation of CPO is a major concern in the palm oil industry especially accumulation of FFA. Irrespective of the processing method, FFA accumulation could occur at all the unit operation of the palm oil milling process, which consequently affects its quality. Also in order to allow for efficient mitigation strategies of monochloro-propanediol fatty acid esters (MCPDFE) and that of glycidol fatty acid esters (G-FE) in crude and refined palm oil, a robust and analytical study of the whole value chain of oil palm fruit is desired.

It is therefore pertinent to understand the kinetics of this enzyme in its native or crude state as most of the reported studies are done in-vitro using purified or immobilized lipase. To date, there is no data on the thermal effect on endogenous lipase in mesocarp fibre of palm fruit. Hence, the study of FFA accumulation during postharvest activities of fresh oil palm fruits is important to improve CPO quality by understanding the reaction kinetics of enzymatic hydrolysis (lipase) and heat induced hydrolysis.

1.4 Research Objectives

The general objective of this research was to elucidate the process conditions and practices that affect the quality of CPO produced in palm oil mills with a view to gain a better understanding of oil deterioration during the processes.

The specific objectives of this study were:

- i. To evaluate and model the effects of mechanical damage/bruise, storage/delay time and temperature on FFA accumulation in the fruits mesocarp of oil palm fruitlets.
- ii. To model and simulate heat penetration and distribution in oil palm fruitlets during heat treatment process.
- iii. To develop the reaction kinetics model of thermal inactivation of endogenous lipase responsible for the accumulation of FFA in bruised OPF using partial differential equation.
- iv. To develop the reaction kinetics of thermal-induced hydrolysis of crude palm oil with heat and mass transfers in a closed system.

1.5 Significance and scope of study

The main quality parameter of CPO for both human consumption and industrial use is FFA content. Therefore, the scope of this research is limited to laboratory-scale study of pre-milling and milling factors that lead to the accumulation of FFA in the extracted CPO and to develop a dynamic model for the kinetics of FFA accumulation in bruised fruits, in-vivo activity of the endogenous lipase (thermal inactivation) and thermal induced hydrolysis of TAG. The knowledge of the mechanisms in which lipase hydrolyses TAG and its thermodynamic parameters are essential for the development of rational approaches to enzyme inactivation. While the kinetics of quality changes (FFA accumulation) in CPO during processing of OPF will enable prediction of final quality of the product and provides a scientific tool for the improvement of the process through correct selection of process conditions that will enhance quality control and help in formulation of mitigation strategy towards curbing the formation of precursor of 3-MCPD in CPO during the downstream process of CPO production.

1.6 Outline of the study

This thesis is organized into seven Chapters. Chapter one explains the background of the research, providing an overview of palm fruit processing and the research gap in the study of oil palm fruits along with the objectives set to be achieved in the study. Literature related to the variety of palm fruit, harvesting and post-harvest activities that lead to FFA accumulation in palm fruits along with milling activities that contribute to FFA accumulation in the extracted CPO were reviewed in Chapter two. Also presented in Chapter two are literature on chemical composition and thermal properties of palm fruit and CPO, hydrolysis of TAG (thermal and enzymatic), its kinetics and

models.

Chapter three is the study of pre-milling factors (bruise, environmental temperature and delay time) on FFA accumulation in OPF. The methodology used, the results and discussions are presented. Also present in this chapter are model development and simulation works carried out to achieve the set objective (objective one).

Chapter four represent the first unit operation in the milling of OPF (heat treatment). Presented in this chapter is the simulation of heat penetration and distribution in the OPF during heat treatment. The procedures used for the simulation and the results are discussed.

Chapter five contains the comprehensive experimental works and model development on inactivation kinetics of the endogenous lipase in OPF. Effects of heat on the abscission layer of OPF, the integrity of the oil globule membrane as well as in-vivo thermal hydrolysis of the TAG are presented and discussed. Also presented in this chapter is the effect of increase in FFA, DAG and MAG on the formation of lipid contaminants such as MCPD-FE and G-FE.

Presented in Chapter six is the study of effect of heat and moisture content on FFA accumulation in the CPO extracted after sterilization. In addition, a detailed dynamic model of kinetics of thermal hydrolysis of CPO in a closed system is also presented.

Chapter seven is the conclusions drawn at the end of the study and suggestions for further research. Figure 1 is the flow diagram/structure of this thesis.

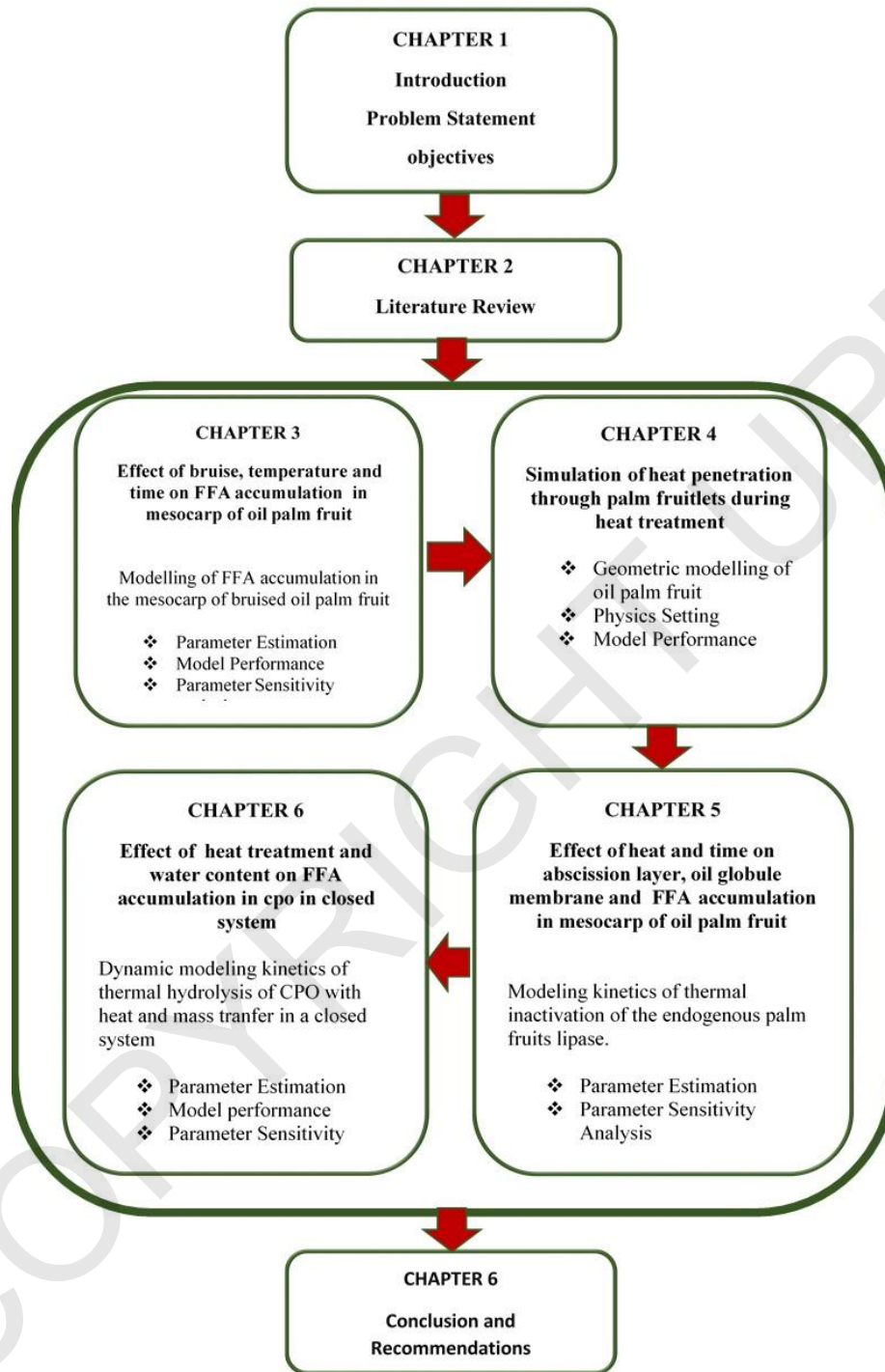


Figure 1.1 : Thesis Structure

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