

**INHIBITION OF FREE FATTY ACID  
FORMATION IN OIL PALM FRUIT  
BY USING BUFFER SOLUTION**

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I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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IN OIL PALM FRUIT BY USING BUFFER SOLUTION**

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## **ABSTRAK**

Asid lemak bebas (ALB) merupakan salah satu kayu ukur yang sering digunakan untuk menilai kualiti minyak sawit. Ia terhasil daripada reaksi hidrolisis trigliserida (TG) iaitu komponen utama di dalam minyak sawit. Kewujudan ALB akan menyebabkan kualiti minyak merosot dan juga berbau tengik. Had kepekatan ALB yang dibenarkan dalam minyak sawit mentah (MSM) adalah 5% wt. Sekiranya melebihi kepekatan yang ditetapkan, maka ia perlu disingkirkan di kilang penapisan dan ini akan dianggap sebagai kerugian minyak. Bagi melihat kecenderungan ALB yang realistik di kilang kelapa sawit, kesan kaedah penyimpanan TBS pada hidrolisis oleh lipase mesokarp terhadap buah kelapa sawit juga telah dikaji selama seminggu. Kandungan ALB dari sampel luar didapati bertentangan dengan peningkatan trend berayun yang ditunjukkan oleh sampel dalam. Sampel dalam secara amnya menunjukkan trend yang meningkat seperti yang dijangka. Model-model tersebut paling sesuai digunakan pada persamaan sinusoidal di mana nilai  $R^2$  untuk tahun 2003, 2007 dan 2015 masing-masing adalah 0.95, 0.62 dan 0.84. Sementara itu, sampel luar menunjukkan trend penurunan ALB dan dimasukkan ke dalam persamaan sigmoidal dan sinusoidal. Nilai  $R^2$  masing-masing adalah 0.48, 0.89 dan 0.77. Walau bagaimanapun, kandungan gliserida dari kedua-dua kaedah tersebut meningkat dalam kenaikan atau daya eksponen setelah seminggu disimpan. Ini menunjukkan bahawa faktor kelembapan menjadi reaktan penghad. Tiada trend konklusif yang dapat dirumuskan untuk kandungan minyak dan ALB berdasarkan usia pokok kelapa sawit. Kaedah semasa dalam mengawal pembentukan ALB adalah dengan pensterilan tanda buah segar (TBS) pada suhu dan tekanan tinggi. Walau bagaimanapun, keadaan dan susunan TBS yang sangat padat akan menyebabkan haba tidak dapat dipindahkan secara seragam dan penyingiran ALB menjadi tidak lengkap. Kajian ini bertujuan untuk menerapkan dua jenis larutan penyangga sebelum proses penceraaan untuk meningkatkan pengurangan ALB. Faktor-faktor yang mungkin mempengaruhi tindak balas telah dikaji menggunakan reka bentuk faktorial dengan menganalisis perbezaan kepekatan ALB. Ini termasuk kepekatan larutan penyangga di mana julatnya adalah 1–10 mM untuk larutan penyangga asetat atau 1–20% w/v untuk larutan penyangga natrium silikat, jumlah larutan penyangga bermula dari 10 hingga 250 ml per 100 g dan masa penceraaan antara 35 ke 60 minit. Secara keseluruhannya, larutan penyangga telah memberikan kesan positif terhadap penurunan ALB. Kedua model adalah signifikan di mana nilai  $R^2$  untuk penyangga asetat adalah 0.85 sementara untuk natrium silikat,  $R^2$  adalah 0.88. Larutan penyangga asetat pada kepekatan 1 mM sangat mempengaruhi pembentukan ALB dengan mengurangkannya hingga 14% v/v. Walaupun kepekatan larutan tidak signifikan bagi larutan penyangga natrium silikat, interaksi antara kepekatan dan jumlah larutan mampu mengurangkan pembentukan ALB dengan ketara di mana perbezaan sekitar 30% v/v telah dicapai. Ini dapat disimpulkan berdasarkan tiga prinsip asas: penyahaktifan lipase kerana keadaan pH yang melampau, mengekalkan reaksi keseimbangan dengan menambahkan asid karboksilik ekstrinsik dan peneutralan ALB dengan menggunakan larutan alkali. Penyelidikan lebih lanjut dicadangkan untuk memperincikan analisis sekiranya ekstrak mengandungi produk sampingan lain.

## ABSTRACT

Free fatty acid (FFA) is one of the indicators commonly used in evaluating palm oil quality. It is produced from the hydrolysis reaction of triglyceride (TG), the main constituent of palm oil, and the presence degrades the oil quality due to rancidity. The allowable limit of FFA in crude palm oil (CPO) is 5% wt; otherwise, it will be removed during refinery and be regarded as oil losses. Current method in controlling the FFA formation is by sterilization of fresh fruit bunches (FFBs) at high temperature and pressure. However, due to the closed-packed arrangement of FFBs, heat may not uniformly be distributed, causing incomplete inhibition of FFA. To observe a realistic FFA trend in oil palm mills, the effects of FFBs storage method on hydrolysis by mesocarp lipase in oil palm fruits were studied as well, for a week. Besides that, this study aims to enhance the FFA reduction by applying two types of buffer solution before the digestion step. Factors that are likely affecting the reaction were studied using the factorial design by analyzing the FFA concentration difference. These include buffer concentration whereby the ranges is 1–10 mM for acetate or 1–20% w/v for sodium silicate, buffer loading from 10 to 250 ml per 100 g and digestion time between 35 to 60 minutes. FFA content from outdoor samples contradicts the increased oscillatory trend shown by indoor samples. The indoor samples generally show an increasing trend as expected. The models were best fitted into damped sine equation whereby the  $R^2$  values for 2003, 2007 and 2015 are 0.95, 0.62 and 0.84, respectively. Meanwhile, the outdoor samples show the downward trend of FFA and were fitted into sigmoidal and damped sine equations. The  $R^2$  values are 0.48, 0.89 and 0.77, respectively. However, both methods' glyceride content increased in exponential rise or power after a week suggesting moisture as a limiting reactant. There was no conclusive trend in oil and FFA contents based on the age of the oil palm tree. For second objective, acidic or basic buffer had been applied on the palm mesocarp to compare the FFA content in both sample and blank. Overall, positive effects on FFA inhibition by buffer solutions were observed. The models are significant in which the  $R^2$  values for acetate buffer is 0.85 while for sodium silicate, the  $R^2$  is 0.88. Acetate buffer at 1 mM concentration had strongly affected the FFA formation by reducing up to 14% v/v. Although the buffer concentration alone was not significant for sodium silicate buffer, the interaction between buffer concentration and buffer loading had significantly reduced the FFA formation in which around 30% v/v difference was achieved. These were concluded based on three basic principles: lipase deactivation due to extreme pH conditions, maintaining the equilibrium reaction by adding extrinsic carboxylic acid and neutralization of FFA by using a basic solution. The use of buffer solutions in palm oil mill potentially reduces the oil losses during the refinery. However it is suggested to have further investigation to delineate the presence of any other by-products in the extract.

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