



UNIVERSITI PUTRA MALAYSIA

***EFFECT OF PROCESS VARIABLES IN SUPERCRITICAL CARBON
DIOXIDE EXTRACTION OF TOCOTRIENOLS FROM PALM FATTY ACID
DISTILLATE***

NAJWA BINTI OTHMAN

FSTM 2022 7



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DISTILLATE**

By

NAJWA BINTI OTHMAN

**Thesis Submitted to the School of Graduate Studies,
Universiti Putra Malaysia, in Fulfilment of the
Requirements for the degree of Master of Science**

December 2021

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DEDICATION

This thesis is dedicated to

My supportive parents,

My husband, family, and not to forget

To all my friends.

For their unconditional love, prayers and support through this journey.



Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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By

NAJWA BINTI OTHMAN

December 2021

Chair : Norhidayah Binti Suleiman, PhD
Faculty : Food Science and Technology

Palm fatty acid distillate (PFAD) is a by-product of palm oil refineries that have high valuable active compounds, specifically tocotrienols. It is commonly extracted using the conventional method, but, argued for its sustainability with the huge hazardous solvent residues, time consumption, and not suitable for thermo-labile compounds. Alternatively, the green sustainable technology, supercritical carbon dioxide (scCO₂) extraction was employed in this work. Hence, the objectives of this study were to evaluate the effect of main process variables, namely pressure and temperature on the tocotrienols extraction and to determine optimal conditions for the recovery of tocotrienols using scCO₂ extraction. In addition, investigation on the static mode (90 and 180 min) and solvent polarity modification by using single and pair mixtures co-solvent at optimum condition were also carried out to enhance the extraction of tocotrienols. The research began with the optimization process of tocotrienols extraction from pre-treated PFAD using scCO₂ at a temperature range of 40-60 °C and pressure range of 20-40 MPa for a fixed CO₂ mass flow rate of 32 ± 2 g/min and dynamic extraction time of 5 h through the Central Composite Design (CCD) with five replications of the central point. It was found that temperature had the most positive effect on the extraction of tocotrienols. The tocotrienols extraction was proportionally increased to a temperature from 40 up to 50 °C. Further increased temperature to 60 °C lowered the density of scCO₂ hence, reduce the solubility of the interest compound to be extracted. Pressure is also a prominent factor in the extraction of tocotrienols. The predicted best condition (20 MPa and 53 °C) by response surface methodology (RSM) produced 16.45 mg/g of tocotrienols content. Static mode for 180 minutes does significantly improve the recovery of tocotrienols (23.62 ± 0.37 mg/g). The static mode was seen to promote the interest solute transfer through the enhancement of the permeability of cell walls by rupturing the sample. Besides, solvent polarity modification with aided of co-solvents significantly increased the tocotrienols content in the extracts. The content of tocotrienols was approximately double up (30.03 ± 0.03 mg/g) with the addition of 0.075 ml/g ethanol. Following that, the

presence of 0.075 ml/g hydrogen bond donor (HBD)-hydrogen bond acceptor (HBA) pair mixtures co-solvent (isopropanol:acetone) resulted in the highest tocotrienols concentration (33.47 ± 0.29 mg/g). This indicated the chemical and physical interaction between the co-solvent and the interest solute molecule, thus, improved the solubility of tocotrienols in the $scCO_2$ system. In summary, tocotrienols could be extracted from PFAD using $scCO_2$ and further improved with slight modifications to the techniques. The solvent polarity modification of the $scCO_2$ exhibited the best technique to improved the tocotrienols content, which may be related to the wide range of polarities. Herein, ethanol (0.075 ml/g) was chosen to improve the tocotrienols extraction since there were no significantly differences between single co-solvent of ethanol and pair mixtures co-solvent of isopropanol-acetone.

Keywords: Palm fatty acid distillate; Supercritical carbon dioxide extraction; Tocotrienols; Polarity modification; Static-mode extraction

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**KESAN PEMBOLEH UBAH SUPERKRITIKAL KARBON DIOKSIDA
TERHADAP EKSTRAK TOKOTRIENOL DARIPADA SULINGAN ASID
LEMAK SAWIT**

Oleh

NAJWA BINTI OTHMAN

Disember 2021

Pengerusi : Norhidayah Binti Suleiman, PhD
Fakulti : Sains dan Teknologi Makanan

Sulingan asid lemak sawit (PFAD) adalah produk sampingan dari kilang minyak sawit yang mempunyai komponen aktif yang bernilai tinggi, khususnya tokotrienol. Tokotrienol biasanya diekstrak menggunakan kaedah konvensional, tetapi ia bertentangan dengan kelestarian alam seperti penghasilan sisa pelarut bahaya yang banyak, penggunaan masa yang terlalu lama, dan ia tidak sesuai untuk komponen yang termolabil. Sebagai alternatif, teknologi lestari hijau seperti pengekstrakan superkritikal karbon dioksida ($scCO_2$) digunakan dalam penyelidikan ini. Oleh itu, objektif kajian ini adalah untuk menilai kesan pemboleh ubah proses, iaitu tekanan dan suhu pada pengekstrakan tokotrienol dan untuk menentukan keadaan optimal untuk pengekstrakan tokotrienol dengan teknik $scCO_2$. Selain itu, ujikaji terhadap mod statik (90 dan 180 minit) dan pengubahsuaian polariti karbon dioksida dengan menggunakan pelarut tunggal dan pelarut campuran pada keadaan optimal juga dilakukan untuk meningkatkan pengekstrakan tokotrienol. Penyelidikan dimulakan dengan mencari keadaan optimal untuk pengekstrakan tokotrienol daripada PFAD yang telah dihidrolisis menggunakan $scCO_2$ pada julat suhu 40-60 °C dan tekanan 20- 40 MPa serta pada aliran jisim tetap CO_2 32 ± 2 g/min dan masa pengekstrakan dinamik selama 5 jam melalui Reka Bentuk Komposit Pusat (CCD) dengan lima ulangan pada titik pusat. Ia didapati bahawa suhu mempunyai kesan yang paling positif terhadap pengekstrakan tokotrienol. Tokotrienol meningkat secara berkadar dari suhu 40 °C hingga 50 °C. Pada suhu tinggi iaitu 60 °C, ketumpatan $scCO_2$ adalah lebih rendah dan ini mengurangkan kelarutan komponen yang akan diekstrak. Tekanan juga merupakan faktor utama dalam pengekstrakan tokotrienol. Dengan menggunakan kaedah permukaan tindak balas (RSM), keadaan optimal telah diramalkan (20 MPa dan 53 °C) dengan menghasilkan 16.45 mg/g kandungan tokotrienol. Mod statik selama 180 minit meningkatkan tokotrienol secara signifikan (23.62 ± 0.37 mg/g). Mod statik dilihat dapat menaikkan pemindahan zat terlarut melalui peningkatan kebolehan telapan dinding sel melalui pemecahan pada sampel. Selain itu, pengubahsuaian polariti pelarut dengan bantuan pelarut dapat meningkatkan kandungan tokotrienol dalam ekstrak. Kandungan tokotrienol meningkat dua kali ganda (30.03 ± 0.03 mg/g) dengan penambahan 0.075 ml/g etanol. Selain itu, 0.075 ml/g pelarut

campuran HBD-HBA seperti isopropanol: aseton menghasilkan tokotrienol yang tinggi (33.47 ± 0.29 mg/g). Ini menunjukkan interaksi kimia dan fizikal antara pelarut dengan molekul zat terlarut, oleh itu kelarutan tokotrienol dalam sistem scCO₂ dapat ditingkatkan. Secara ringkasnya, tokotrienol dapat diekstrak daripada PFAD dengan menggunakan scCO₂ dan sedikit pengubahsuaian dalam teknik scCO₂. Pengubahsuaian polariti pelarut scCO₂ merupakan teknik terbaik untuk meningkatkan kandungan tokotrienol yang mungkin berkaitan dengan pelbagai julat polariti. Di sini, etanol (0.075 ml/g) telah dipilih untuk meningkatkan pengekstrakan tokotrienol kerana terdapat perbezaan yang tidak signifikan antara etanol dan pelarut campuran, isopropanol-aseton.

Kata kunci: Sulingan asid lemak sawit; Superkritikal karbon dioksida; Tokotrienol; Pengubahsuaian polariti; Pengekstrakan mod-statik



ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious, the Most Merciful. All praise is only for Allah. With His mercy and guidance, I am so grateful that being so blessed with strength, patience and faith along completing this research journey. No word can describe this feeling when this thesis is successfully materialized. Indeed, with every hardship, there is ease. I would like to express my sincere gratitude and appreciation to my great and kind supervisor, Dr Norhidayah Binti Suleiman, for her patience, motivation, inspiration, and encouragement throughout my challenges in completing this study. I would like to express my appreciation to my co-supervisors, Associate Professor Dr Chong Gun Hean and Dr Ezzat Binti Mohamad Azman for their contributions towards the success of completing this research. May Allah bless them and repay their kindness. I want to thank all the lecturers, officers, and staff for the technical support and facilities provided especially at Faculty of Food Science and Technology, Universiti Putra Malaysia. I owe a special thanks to my beloved parents, Mr Othman Md Lazim and Mrs Khalijah Mohamad, my husband, Mr Ahmad Aizuddin Faiz and my family, for their endless support, prayers, and encouragement. Not forgotten, sincere thanks to all those who indirectly contribute to this research. Finally, acknowledgements credited to Universiti Putra Malaysia for financial support.

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

Norhidayah Binti Suleiman, PhD

Senior Lecturer
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Chairman)

Chong Gun Hean, PhD

Associate Professor
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Member)

Ezzat Binti Mohamad Azman, PhD

Senior Lecturer
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Member)

ZALILAH MOHD SHARIFF, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 19 May 2022

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LIST OF ABBREVIATIONS

PFAD	Palm fatty acid distillate
FFA	Free fatty acid
scCO ₂	Supercritical carbon dioxide
SFE	Supercritical fluid extraction
SCF	Supercritical fluid
CPO	Crude palm oil
T3	Tocotrienols
T	Tocopherols
GDP	Gross domestic product
PKO	Palm kernel oil
MPOC	Malaysia
MPOB	Malaysia Palm Oil Board
IV	Iodine value
PV	Peroxide value
SV	Saponifiable value
RBD	Refined, bleached, and deodorized
AV	Acid value
FAD	Fatty acid distillate
RSM	Response surface methodology
CCD	Central composite design
KT	Kamlet-Taft
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
HPLC	High-performance liquid chromatography
RP-LC	Reverse phase liquid chromatography
PF ₅	Pentafluorophenyl

CHAPTER 1

INTRODUCTION

1.1 Overview

By-product is a secondary product or waste that is derived from the manufacture or production of a primary product. It can be categorized as agricultural or forestry waste, sewage, manure, sawdust or food scraps (Jablonský et al., 2018). Approximately, in a year, 998 million tons of agriculture waste was produced globally and Malaysia recorded about 1.2 million tons per year that disposed into landfills (Ali, 2020). About 77% of agriculture waste is from oil palm industries and the remaining are from rice residues, forestry residues, rubber, cocoa, and coconut (Hamzah et al., 2019). It has been reported, 75% of palm oil waste are from plantation sites which are oil palm fronds (OPF) and oil palm trunks (OPT) and the remaining 25% from mill sites in form of empty fruit bunch (EFB), mesocarp fibre (MF), palm kernel shell (PKS), and palm oil mill effluent (POME) that produced during the extraction of palm oil from fruit bunch (Hamzah et al., 2019).

Proper management of the by-product from industries will help to initiate the entire life cycle of the circular economy concept through reuse/ recycle medium to support zero waste while generating advantages on both environment and economy at the same time (European Commission, 2020). Improper waste management may cause environmental risk specifically high amounts of gases such as N_2O , SO_2 , CH_4 and smoke are generated which can pollute the air, besides, improper waste management may cause water and soil deterioration which can risk human health (Hsu, 2021; He et al., 2019). Proper waste management via reuse or recycle can be beneficial to environmental protection (He et al., 2019). Waste from the palm oil industry can be transformed into a useful product such as biogas, animal feed, soil fertilizer, fermentation media, and yeast production (Zuber et al., 2019). According to Zuber et al. (2019) and Estiasih et al. (2013), the oil residue from palm oil refining of main treatment of POME known as palm fatty acid distillate (PFAD), contains high free fatty acid (FFA) and other valuable bioactive compounds such as vitamin E, phytosterols and squalene.

Interestingly, retaining the availability of bioactive compounds until the manufacturing of the final product is important. Extraction is one of the critical stages in the recovery or valorization of bioactive compounds for any processing or manufacturing plant, irrespective of the product category. Recently, various extraction techniques have been introduced for the recovery of interesting compounds. Extraction techniques include liquid-liquid extraction, solid-phase extraction, solid-liquid extraction, and supercritical extraction. According to Patel et al. (2019), in the extraction process, the sample mixture is separated by dissolving each component with solvents which result in a two-phase- raffinate phase and extract phase. The extraction process was set based on operations (batch or continuous process) and type of phase. Furthermore, the condition of the extraction can have a significant, negative impact on its operating efficiency or quantity and quality of the interest compounds.

Significant research into the extraction or valorization of bioactive compounds from by-products has been conducted over the past century however in recent times this has increased. A Web of Science survey of articles published between 2000 and 2020 showed that of the 207 containing the word 'extraction' in the title, abstract or author-specific keywords, 202 related to food by-product. Similarly, 104 containing the word 'bioactive compounds', 371 related to the food by-product. This gives a proportion of interest in the extraction of bioactive compounds from a by-product.

In this Thesis, there are two studies of tocotrienols extraction. The first part of this thesis is to determine the favourable extraction condition. In particular, the main focus is on the study of main operating conditions (pressure and temperature) relevant to the extraction of tocotrienols using supercritical carbon dioxide (scCO₂). The second part of this Thesis is enhancing the efficiency of tocotrienols extraction using scCO₂ by modifying the scCO₂ system and altering the polarity of CO₂ at optimal conditions. Specifically, the work focuses on the static-dynamic mode extraction and addition of single or pair mixtures of co-solvents. A more detailed explanation of this optimization of scCO₂ process conditions for tocotrienols extraction and modification on scCO₂ for the enhancement tocotrienols extraction is explained in Chapter 4. In summary, this thesis describes the application of scCO₂ for the extraction of tocotrienols from a by-product of palm oil.

1.2 Problem statement

An increasing number of global issues on industrial waste management is alarming. Hence, transforming the industrial by-product into valuable products is necessary to generate zero waste using green sustainable technology. Widely used conventional methods are nevertheless somewhat controversial, as major drawbacks have been reported. The main challenge of these conventional extractions is required longer extraction time, conducted at high temperature, low selectivity of the interest compounds, and non-environmentally friendly. Steam- or hydro- distillation is a traditional extraction technique that has been commonly used to extract essential oils or bioactive compounds from many sources. Technically, this technique does not involve any organic solvents. Nevertheless, this technique is required to be conducted at high temperatures whereas temperature is a major factor that influences the extraction condition of bioactive compounds in this technique. Therefore, the main limitation of this technique is not suitable for thermolabile compound extraction as most volatile components will be degraded and lost by heat at high temperatures. In regards, the high temperature employed is another limitation affecting the quality of the final product since tocotrienols can easily degrade at high temperatures.

Soxhlet extraction has widely been used to extract bioactive compounds from various sources for the past century (Weggler et al., 2020; Rakhee et al., 2018). The Soxhlet extraction method is time-consuming, as it takes from several hours up to several days. The prolonged extraction time can cause the degradation of unsaturated or ester compounds and volatilization of the bioactive compounds through thermal or hydrolytic effects, hence, reduce the quality of the extracts. In addition, the low selectivity of the

interest compounds is another limitation of this conventional method. High selectivity of interest compounds can be achieved by choosing the right solvent based on the polarity of targeted compounds (Tzanova et al., 2020). Per law, the similarity and intermiscibility, a solvent with a polarity value close to the polarity solute are expected to deliver better results and vice versa. Besides, organic solvents are categorized as conventional extraction methods is widely used in many industries for tocotrienols production. The use of hazardous solvents such as hexane and chloroform are harmful to health, products, and the environment. The high consumption of harmful solvents and the management of the industrial waste contributes to the environment, hence, increase the production costs resulting in the production viable conventional method is no longer sustainable.

Recently, several technologies pairing green technology with a green chemistry solvent were developed for the recovery of one or a few target compounds from samples using a single process. Particularly for the recovery of the vitamin E family, researchers have focused on alternative extraction techniques. This study will focus primarily on supercritical fluid extraction (SFE) with the use of carbon dioxide as a solvent is a greener alternative to the conventional extraction method. Due to its superior properties, it can be applied to food and pharmaceutical applications. However, the capability of scCO₂ to extract moderate polar compounds is limited since CO₂ is a non-polar solvent. The efficiency of the extraction can be improved through the solubility of polar compounds in the separation process by a slight modification of the technique and altering the polarity of the system.

1.3 Objectives

The primary objective of this thesis is to assess the efficiency of scCO₂ with possible available techniques in the extraction of tocotrienols in PFAD. The specific aims to achieve the main objective were to:

1. Evaluate the impact of pressure and temperature of scCO₂ on the yield of tocotrienols extraction from PFAD.
2. Determine the optimal condition for the recovery of tocotrienols from PFAD by using central composite design (CCD).
3. Utilize and extend available techniques in scCO₂ to monitor the impact and effectiveness of the recovery of tocotrienols in a range of conditions.

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