



**UNIVERSITI PUTRA MALAYSIA**

***OPTIMIZATION AND MATHEMATICAL MODELING OF GREEN  
SOLVENT-MEDIATED EXTRACTION OF ESSENTIAL OIL FROM *Citrus  
hystrix* DC. LEAVES***

**NOOR AMIRAH BINTI ABDUL HALIM**

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By

**NOOR AMIRAH BINTI ABDUL HALIM**

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

**July 2022**

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*This thesis is fondly dedicated to my beloved late father, Abdul Halim, who has always been my source of strength despite his absence, my dearest mother Noor Sidah for her never-ending loves and prayers, and my darling husband Wan Shuhairi for his unconditional support throughout this journey.*

*'The only true wisdom is in knowing you know nothing'  
-Socrates-*

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

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July 2022

**Chair : Prof. Zurina Zainal Abidin, PhD**  
**Faculty : Engineering**

*Citrus hystrix* DC. leaves or Kaffir lime leaves is known for its prominent organoleptic properties and therapeutical functionalities but are still underutilized as a source for the high-demand citrus-based essential oil (EO), due to the limitation of conventional hydrodistillation (HD) method that results in low yield. Green solvents such as natural deep eutectic mixture and subcritical-phase water described in previous studies not only improved the bioproduct extraction but also friendlier to the environment. However, the use of a natural deep eutectic solvent (NADES) requires correct formulation to be effective, while adopting water at subcritical conditions can affect the quality of EO. Hence, in this work, the application and the effectiveness of natural deep eutectic solvent-assisted hydrodistillation (NADES-HD) and subcritical water extraction (SWE) methods were comparatively studied.

Based on screening and optimization studies, NADES-HD and SWE techniques successfully improved the EO yield by twice (1.32% w/w), and almost fourfold (2.14% w/w) respectively, in comparison to conventional HD (0.57% w/w) at their corresponding optimum extraction conditions. Both methods were well-fitted to the one-site kinetic desorption model at an extraction rate ( $k$ ) of 0.0107 to 0.0136 min<sup>-1</sup> and 0.0224 to 0.0463 min<sup>-1</sup> for NADES-HD and SWE, respectively. Assessment of the mass transfer behavior estimates that the effective diffusivity, ( $D$ ) values for NADES-HD and SWE corresponded to 3.68 x 10<sup>-6</sup> to 5.59 x 10<sup>-6</sup> cm<sup>2</sup>/s and 8.91 x 10<sup>-8</sup> to 1.47 x 10<sup>-7</sup> cm<sup>2</sup>/s, respectively, and obeys the Fick's second law of diffusion. Meanwhile, for thermodynamics behavior, both methods were identified as exergonic and spontaneous processes with the free Gibbs energy ( $\Delta G$ ) values ranging from 6.83 to 8.73 kJ/mol for NADES-HD and 2.23 to 4.74 kJ/mol for SWE.

The chemical profile analysis revealed that the SWE produced more EO compounds, where isopulegol (52.21%) was the predominant constituent, meanwhile NADES-HD

has yielded EO that is rich in citronellal (75.99%), similar to conventional HD (75.04%). Besides, SWE-extracted EO exhibited a superior antioxidant activity while the EO extracted by NADES-HD demonstrated a better antimicrobial activity. The physical characterization of the post-extraction leaves samples indicated that the lignocellulosic structures of SWE-extracted leaves were severely disrupted compared to the damages observed on NADES-HD and conventional HD samples, hence implying the reason for the higher EO yield obtained by the SWE process. In brief, NADES-HD and SWE are the potential alternatives to conventional HD, where the quantity and quality of EO could be enhanced within a shorter extraction time and at the same time could minimize the energy requirement.



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

**PENGOPTIMUMAN DAN PEMODELAN MATEMATIK BAGI  
PENGEKSTRAKAN-PERANTARAAN PELARUT HIJAU MINYAK PATI  
DARI DAUN *Citrus hystrix* DC.**

Oleh

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Daun *Citrus hystrix* DC. atau daun limau purut terkenal dengan ciri-ciri organoleptik dan fungsi terapeutik yang ketara, namun masih kurang digunakan sebagai sumber minyak pati (EO) berasaskan sitrus yang mempunyai permintaan tinggi, disebabkan oleh penghadan kaedah penyulingan hidro (HD) konvensional yang menghasilkan hasil yang rendah. Pelarut hijau seperti campuran eutektik dalam semulajadi dan air pada fasa di bawah suhu kritikal yang diterangkan dalam kajian-kajian terdahulu bukan sahaja dapat meningkatkan pengekstrakan bioproduk tetapi juga lebih mesra alam. Walau bagaimanapun, penggunaan pelarut eutektik dalam semulajadi (NADES) memerlukan formulasi yang betul untuk menjadikannya berkesan, manakala penggunaan air pada keadaan di bawah suhu kritikal boleh menjejaskan kualiti EO. Oleh itu, dalam kajian ini, aplikasi dan keberkesanan penyulingan hidro berbantuan pelarut eutektik dalam semulajadi (NADES-HD) dan kaedah pengekstrakan oleh air di bawah suhu kritikal (SWE) telah dikaji secara perbandingan.

Berdasarkan kajian saringan dan pengoptimuman, teknik NADES-HD dan SWE masing-masing berjaya meningkatkan hasil EO sebanyak dua kali ganda (1.32% b/b), dan hampir empat kali ganda (2.14% b/b), berbanding HD konvensional (0.57% b/b) pada keadaan pengekstrakan optimum yang sepadan. Kedua-dua kaedah adalah sesuai dengan model nyah serapan kinetik satu kawasan, pada kadar pengekstrakan ( $k$ ) masing-masing, iaitu 0.0107 hingga 0.0136  $\text{min}^{-1}$  dan 0.0224 hingga 0.0463  $\text{min}^{-1}$  bagi NADES-HD dan SWE. Penilaian berkenaan tingkah laku pemindahan jisim, menganggarkan bahawa nilai-nilai resapan berkesan, ( $D$ ) untuk NADES-HD dan SWE masing-masing sepadan dengan  $3.68 \times 10^{-6}$  hingga  $5.59 \times 10^{-6} \text{ cm}^2/\text{s}$  dan  $8.91 \times 10^{-8}$  hingga  $1.47 \times 10^{-7} \text{ cm}^2/\text{s}$ , dan mematuhi hukum resapan kedua Fick. Sementara itu, bagi tingkah laku termodinamik, kedua-dua kaedah telah dikenal pasti sebagai proses eksergonik dan spontan, dengan nilai tenaga Gibbs bebas ( $\Delta G$ ) antara 6.83 hingga 8.73 kJ/mol untuk NADES-HD dan 2.23 hingga 4.74 kJ/mol untuk SWE.

Analisa profil kimia mendedahkan bahawa SWE menghasilkan lebih banyak sebatian EO, di mana isopulegol (52.21%) adalah jujuk utama, manakala NADES-HD telah menghasilkan EO yang kaya dengan sitronelal (75.99%) menyamai dengan HD konvensional (75.04%). Selain itu, EO yang diekstrak oleh SWE mempamerkan aktiviti antioksidan yang unggul manakala EO yang diekstrak oleh NADES-HD menunjukkan aktiviti antimikrob yang lebih baik. Pencirian fizikal sampel daun selepas pengekstrakan menunjukkan bahawa struktur lignoselulosa daun yang diekstrak oleh SWE telah terjejas teruk berbanding dengan kemusnahan yang diperhatikan ke atas sampel-sampel NADES-HD dan HD konvensional, justeru menjelaskan sebab bagi hasil EO yang lebih tinggi diperolehi oleh SWE. Secara ringkasnya, NADES-HD dan SWE merupakan alternatif-alternatif yang berpotensi kepada HD konvensional, di mana kuantiti dan kualiti EO boleh dipertingkatkan dalam masa pengekstrakan yang lebih singkat dan pada masa yang sama dapat meminimumkan keperluan tenaga.





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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

ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CCD	Central composite design
DES	Deep eutectic solvent
DES-HD	Deep eutectic solvent assisted hydrodistillation
DPPH	2,2-diphenyl-1-picrylhydrazyl
EO	Essential oil
FTIR	Fourier transform infra-red
GC-MS	Gas chromatography-mass spectroscopy
HD	Hydrodistillation
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
NADES	Natural deep eutectic solvent
NLSF	Nonlinear squared fitting
RSM	Response surface methodology
SD	Steam distillation
SEM	Scanning electron microscopy
SSR	Sum of squared residual
SWE	Subcritical water extraction

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

Plant essential oils (EOs) are known for various benefits, particularly their organoleptic and bioactive properties. Complex chemical compositions, which are predominantly composed of terpenic compounds give synergy of biological effects to the EOs, offering a broad spectrum of bioactivities. The demand for EOs especially for citrus-based oil by the food industry has increased in line with the diversity of the functionality of EOs, particularly in food flavoring and preservation (Giacometti et al., 2018; Tongnuanchan and Benjakul, 2014). Among the EOs, citrus-based EOs dominate the global market demand due to their strong organoleptic properties, notable bioactive functionalities, a vast array of applications, and sturdy demand dynamics (Gonçalves et al., 2018; Mustafa, 2015).

*Citrus hystrix* (*C. hystrix*) or generally known as Kaffir lime is an aromatic perennial plant that native to South-East Asia. The leaves and the fruits are commonly used as culinary herbs to improve the organoleptic properties of food, as well as a traditional remedy for various illnesses (e.g., digestive aid, blood cleansing, cold, congestion, and cough). The leaves of *C. hystrix* are unique among citrus varieties and, for some particular applications, are more pronounced than the fruits due to its significant organoleptic characteristic (Wongpornchai, 2012). The EO extract of *C. hystrix* leaves has been revealed to have notable bioactivities such as antioxidant, antibacterial, antimicrobial, antileukemic, and antitussive properties (Dilla Dertyasasa and Anindito Sri Tunjung, 2017; Md Othman et al., 2016; Norkaew et al., 2013). These features make *C. hystrix* leaves promising sources that can satisfy the increasing demands on citrus-based EO in numerous applications, particularly in food flavoring and fragrance formulation, cosmetic, pharmaceutical, and household products.

EOs are generally extracted by hydrodistillation (HD) and steam distillation (SD) methods due to their practicability and being economically viable. However, HD is a time-consuming process that always leads to multiple unfavorable consequences, including low production yield. The amount of EO in plants only contains about 0.01% to 10% of the total mass, depending on the plant parts (Giacometti et al., 2018). Due to this small proportion, the extraction process is a crucial aspect influencing the quantity and quality of the EOs. Thus, alternatives in EO extraction are continually upgraded to improve extraction efficiency. In HD, the distillation mechanism enabled the use of water as the extraction medium for nonpolar EO compounds. This has become a better alternative to organic solvent extraction and thus, fulfills the criterion of the green extraction approach. Besides, the use of water is undeniably favorable for EO extraction in order to ensure the safety aspect of the product that is vital in food, nutraceutical, and pharmaceutical manufacturing.



However, the solubility of water is limited by its high polarity characteristic, which restricts the solubilization of nonpolar EO compounds. Due to this factor, innovations in the extraction protocol involving water as the extraction medium are worth to be explored. Hence, the applicability of emerging green solvents such as deep eutectic mixtures and the use of water at the subcritical phase for EO extraction has been the subject of interest in this study. The efficiency of EO extraction could be enhanced by the assistance of the natural deep eutectic solvent (NADES), a harmless supramolecule solvent made of hydrogen bond-donor (HBD) and hydrogen bond-acceptor (HBA) (Vilková et al., 2020). Meanwhile, the limitation of highly polar water during non-polar EO extraction can be overcome by pressurizing water enough to maintain its liquid state while ensuring a high temperature above its atmospheric boiling point ( $>100\text{ }^{\circ}\text{C}$ ) and below its critical point ( $<374\text{ }^{\circ}\text{C}$ ) (Plaza and Turner, 2015).

## 1.2 Problem Statement

Increasing awareness among consumers of the therapeutic properties of EOs triggers a growth trend in the current EO market with citrus-based EO being the leading segment. Most of the citrus-based EOs that dominate the global market are mainly obtained from the peels of citrus fruits (González-Mas et al., 2019; Mustafa, 2015) which predominantly consist of limonene, a hydrocarbon monoterpene fraction. The high content of this fraction is usually undesirable, requiring a subsequent 'deterpenation' process to concentrate the oxygenated fractions to improve the oil quality and its storage stability (Luque De Castro et al., 1999; Mustafa, 2015). On the contrary, *C. hystrix* leaves EO has primarily consisted of citronellal, an oxygenated monoterpene, which is a desirable fraction of EO (Phanthong et al., 2013; Wongpornchai, 2012). Oxygenated monoterpenes are always preferable due to their superior flavor, and highly odoriferous characteristics (Ferhat et al., 2007; Liu et al., 2018) compared to hydrocarbon monoterpenes, which are prone to deterioration and the possibility of producing undesirable compounds that can affect the flavor and aroma of the oils (Gonçalves et al., 2018; Luque De Castro et al., 1999). Therefore, a higher proportion of oxygenated monoterpene in the *C. hystrix* leaves EO would be advantageous against the conventional citrus oils.

The isolation of EO is implemented conventionally by HD and SD. However, this method suffers from several drawbacks, such as being time-consuming, which leads to high energy consumption, uneven heat distribution, and low production yield (Solanki et al., 2018). A lengthy operation would demand a high energy consumption for the heating and cooling of water at elevated temperatures. It has been found that the industrial extraction process by distillation uses about 50% of the energy of the whole industrial process, which could have a significant environmental impact (Chemat et al., 2012). Besides, prolonged contact between analytes and heated water can cause degradation and alteration of the compounds, affecting the quantity and quality of the EOs (Asbahani et al., 2015; Cook and Lanaras, 2015). Worse still, the yield of EO produced is frequently low and always requires a massive amount of plant materials to produce a reasonable volume of EO (Chemat et al., 2012; Liu et al., 2018). According to the literature, the average yield of *C. hystrix* leaves EO extracted using HD were lesser than 1% (Kasuan et al., 2009; Yahya et al., 2018). Despite the limitations, the use of water as a green extraction medium in the conventional HD method is regarded as highly advantageous

for the extraction of EO compounds. Therefore, the innovations in the extraction procedure employing inherently safer extraction mediums such as water, with potency to improve the EO extraction yield are indeed desirable.

NADES with its unique physicochemical properties could potentially use as the co-solvent to water in HD, to aid the release of EO compounds, by enhancing the disruption of the plant's cellular matrixes. According to Flamini et al.(2015) and Solanki et al. (2019), the ionic-based solvent can dissolve the lignocellulosic barrier in plant cellular matrices, hence enhancing the release of more EO compounds. On another note, water under a subcritical phase has tunable physicochemical properties that can enhance its solubilization capacity on less polar compounds (Plaza and Marina, 2019; Teo et al., 2010). The efficacy of subcritical water extraction (SWE) in EO extraction has been proven in several studies (Khajenoori et al., 2015, 2013; Samadi et al., 2020, 2019). Plaza and Marina (2019) have also claimed that subcritical condition allows modification of the water's dielectric constant and polarity, facilitating a better extraction of compounds by improving the mass transfer rate. Thereby, NADES-assisted HD and SWE could offer an alternative method to conventional HD, which can still exploit the advantages of green solvent but with an improved extraction efficiency.

The application of NADES-assisted HD and SWE approaches in the extraction of *C. hystrix* leaves or another citrus-based EO has not been reported in the literature to date. Thus, the effectiveness and capacity of these procedures as an alternative in enhancing the yield of *C. hystrix* leaves EO was uncertain since the knowledge of the influence of extraction factors, the optimal operational conditions, as well as the kinetic behavior, were still indeterminate. The application of NADES in HD procedures has never been reported elsewhere, thereby the industrial application of this innovation would never be achieved without the preliminary experimental data. However, in terms of an economic perspective, the production cost of NADES has been predicted to be only 20% of the ionic liquid (Xu et al., 2016). Hence, this could be the added value to the NADES-HD as it can be considered an economical approach to EO extraction. Besides, according to Reyes-Jurado et al.(2014), the chemical profile of EO extract is significantly affected by the extraction method, hence the investigation of the chemical profiles of *C. hystrix* leaves EOs yielded from NADES-HD and SWE is crucial as it possibly exhibits different bioactivities that might influence the quality of the EO. In fact, the implications of both extraction procedures in terms of quantity and quality, relative to the conventional practice were also unknown. Thereby, this study was initiated to fill these voids as both of the innovations are perceived as among the potential alternatives to improve the extraction efficiency of *C. hystrix* leaves EO in order to meet the growing demand for end-use product manufacturing.

### 1.3 Objectives of Study

This study is conducted to investigate the effectiveness, efficacy, and efficiency of an innovative green-solvent-mediated extraction approach through NADES-HD and SWE procedures in order to enhance the quantity and quality of the EO from *C. hystrix* leaves. Thus, the specific aims of the study are;



- (i) To investigate the factors influencing the EO yield from *C. hystrix* leaves extracted through NADES-HD and SWE procedures.
- (ii) To obtain the optimal extraction conditions and establish the empirical regression models for the extraction of EOs from *C. hystrix* leaves for both NADES-HD and SWE procedures.
- (iii) To assess the kinetics, mass transfers and thermodynamics behaviors of *C. hystrix* leaves EO extraction through NADES-HD and SWE procedures.
- (iv) To elucidate and compare the physicochemical effects of NADES-HD and SWE procedures on the characteristics of the isolated EOs, and the leaves structures relative to the conventional HD.

#### 1.4 Scope and Limitation of Study

This study involved the application of deep eutectic mixture solution and subcritical water as green solvent alternatives employing NADES-HD and SWE procedures, for the extraction of EO from *C. hystrix* leaves. The effectiveness of the extraction methods was investigated through the screening of the extraction parameters, hence the effects of the parameters on EO yield were evaluated. Both methods were then subjected to optimization in order to analyze the efficacy of the procedure to produce the desired outcome. Thus, their kinetic and thermodynamic behaviors were investigated accordingly. Finally, the efficiency of both methods was assessed based on the product (EO) attributes as well as the physicochemical effects of the procedures on the raw material (*C. hystrix* leaves). The efficiency of the NADES-HD and SWE were also evaluated and compared quantitative and qualitatively relative to the conventional HD. Hence, the evaluation of HD procedures only covers the characterization part for comparison purposes.

#### 1.5 Significance of Study

*C. hystrix* leaves could be one of the potential sources that ensure a continuous supply to satisfy the market demand. Not just to sustain the supply, the use of *C. hystrix* leaves also could provide variability in citrus EO products that offer different organoleptic properties and bioactivities than the current-commercialized citrus oil. This study essentially proposed another alternative method for EO extraction using *C. hystrix* leaves as the source. The proposed methods suggest another approach in extraction protocol to improve the EO yield by green solvent-mediated extraction. Hence, the effectiveness of the extraction processes is evaluated. The effects of operational conditions, optimization, kinetic modeling, and characterization process were performed and thoroughly studied. In short, this research might lead to an advancement of knowledge in future studies to improve the low EO yield issue.

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