Optimization, kinetics and thermodynamics model of *Zanthoxylum limonella* essential oil extraction for mosquitoes repelling by hydro-distillation process

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การหาสภาวะที่ดีที่สุดและแบบจำลองทางจลนศาสตร์และอุณหพลศาสตร์ของการสกัดน้ำมันหอมระเหยจากมะแขว่น (*Zanthoxylum limonella*) สำหรับไล่ยุงโดยกระบวนการกลั่นด้วยน้ำร้อน

ไชยวุฒิ แฝงเพ็ชร

ณัฐนันท์ สุขสีทา

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Title	Optimization, kinetics model and thermodynamics of *Zanthoxylum limonella* essential oil extraction for mosquitoes repelling by hydro-distillation process
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Abstract

Ma-khwaen or *Zanthoxylum limonella* (*Z. limonella*) is one of the spices used for traditional medicine treatments due to the active components such as limonene, sabinene, etc., which can be used for mosquito repellent, drug, or therapeutics. In this study, the optimum conditions for *Z. limonella* oil extraction using hydro-distillation process were studied, by varying water to solid ratio (2:1-7:1 mL/g), extraction temperature (130 °C, 140 °C, and 150 °C), and extraction time (20-300 min). Furthermore, three kinetics models for extraction: pseudo-first order kinetics, simultaneous washing and diffusion, and instantaneous washing followed by diffusion were investigated. In addition, the study of thermodynamics parameters for indicating extraction behavior and the predictive thermodynamics method (UNIFAC) to estimate the amount of active components at each temperature were explored. The optimum conditions are 5:1 mL/g of water to solid ratio, extraction temperature of 150 °C, and extraction time of 180 min gave 15.39 ± 0.25%v/w. The simultaneous washing and diffusion kinetics model predicted the most accurate trends when compared with the experimental data. In addition, the activation energy (Ea) for extraction is 17.36 kJ/mol and the differential enthalpy (ΔH) and entropy (ΔS) were positive which indicated that system is endothermic and irreversible. The predictive mole fraction of active components at different temperature using UNIFAC method are very closed to the experimental results for each temperature. For example, at temperature of 150 °C, the prediction of limonene (40.00%), sabinene (33.21%) and others (26.78%) which is very close to the experimental result of limonene (40.47%), sabinene (33.33%), and others (26.20%).

Keywords: hydro-distillation method, *Z. limonella*, kinetics model, thermodynamics model

เรื่อง	การเพิ่มประสิทธิภาพและแบบจำลองทางจลนศาสตร์และอุณหพลศาสตร์ของการสกัดน้ำมันหอมระเหยจากมะแขว่น (*Zanthoxylum limonella*) สำหรับไล่ยุงโดยกระบวนการกลั่นด้วยน้ำร้อน
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บทคัดย่อ

มะแขว่น มีชื่อวิทยาศาสตร์คือ *Zanthoxylum limonella* เป็นหนึ่งในพืชสมุนไพรมีสารออกฤทธิ์หลายชนิด เช่น ลิโมนีน (limonene) ซาบินีน (sabinene) เป็นต้น ซึ่งสามารถใช้ในอุตสาหกรรมยากันยุง ยาหรือการบำบัด ในการวิจัยนี้ศึกษาสภาวะที่เหมาะสมในการสกัดน้ำมันหอมระเหยจากมะแขว่นโดยใช้วิธีการกลั่นด้วยน้ำร้อน ซึ่งมีตัวแปรที่ส่งผลต่อการทดลองได้แก่ สัดส่วนน้ำต่อของแข็ง (2:1-7:1 mL/g) อุณหภูมิที่ใช้ในการสกัด (130 °C, 140 °C, and 150 °C) และเวลาในการสกัด (20-300 นาที) รวมถึงศึกษาแบบจำลองจลนศาสตร์สำหรับการสกัดทั้งหมดสามแบบจำลองประกอบด้วย แบบจำลองสมการอันดับหนึ่งเทียม (model of pseudo-first order kinetics) แบบจำลองของการสกัดที่เกิดขึ้นพร้อมกันสองขั้นตอนคือ ขั้นตอนการชะล้างและขั้นการแพร่ (model of simultaneous washing and diffusion) และแบบจำลองของการสกัดแบบขั้นตอนชะล้างที่เกิดขึ้นฉับพลันต่อเนื่องด้วยการแพร่ (model of instantaneous washing followed by diffusion) และการศึกษาเกี่ยวกับตัวแปรทางอุณหพลศาสตร์เพื่อศึกษาพฤติกรรมของการสกัด รวมถึงการทำนายปริมาณสารออกฤทธิ์สำคัญแต่ละอุณหภูมิ โดยใช้วิธีการทางอุณหพลศาสตร์ (UNIFAC) จากการทดลองพบว่าสัดส่วนน้ำต่อของแข็ง 5:1 mL/g ที่อุณหภูมิ 150 °C และใช้เวลา 180 นาที เป็นสภาวะที่เหมาะสมที่สุดในการสกัด ซึ่งได้ปริมาณน้ำมันหอมระเหยอยู่ที่ 15.39 ± 0.25%v/w สำหรับแบบจำลองที่ให้ค่าใกล้เคียงกับข้อมูลผลการทดลองที่สุดคือ แบบจำลองของการสกัดที่เกิดขึ้นพร้อมกันสองขั้นตอนคือ ขั้นตอนการชะล้างและขั้นการแพร่ นอกจากนี้ ค่าพลังงานกระตุ้น (Ea) สำหรับการสกัดมีค่าเท่ากับ 17.36 kJ/mol และมีค่าเอนทาลปีและเอนโทรปีที่เป็นบวก ซึ่งบ่งชี้ได้ว่าระบบนี้เป็นระบบดูดความร้อนและไม่สามารถผันกลับได้ และค่าทำนายสัดส่วนโมลของสารออกฤทธิ์ที่อุณหภูมิต่าง ๆ โดยใช้วิธี UNIFAC สามารถทำนายค่าได้ใกล้เคียงกับผลการทดลองทั้งสามอุณหภูมิ โดยค่าที่อุณหภูมิ 150 °C คือ ลิโมนีน (40.00%) ซาบินีน (33.21%) และอื่น ๆ (26.78%) ซึ่งมีค่าใกล้เคียงกับข้อมูลจากผลการทดลองดังนี้ ลิโมนีน (40.47%) ซาบินีน (33.33%) และอื่น ๆ (26.20%)

คำสำคัญ: วิธีการกลั่นด้วยน้ำร้อน, มะแขว่น, แบบจำลองจลศาสตร์, แบบจำลองอุณหพลศาสตร์

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CHAPTER I

INTRODUCTION

1.1 Background

Mosquitoes are the most diverse in tropical forest environments [1]. Mosquitoes are important arthropod vector of human diseases, which transmitted malaria, lymphatic, filariasis, and arboviruses such as dengue virus and zika virus [2]. A recent study published in the lancet infectious diseases reported that COVID-19-related changes in social activities led to a decrease in the incidence of dengue during the first year of the epidemic in 2020. A decrease of approximately 36% 2,795,822 in 2020 vs. 1,788,229 in 2021, in the study area in Southeast Asia and Latin America. However, in 2022, the world begins to loosen Covid-19 restrictions, the incidence and prevalence of dengue fever have increased dramatically in many areas. Countries in Southeast Asia, such as Singapore, Philippines, Indonesia, and Thailand, have reported a significant numbers of dengue fever cases. For example, Singapore during the 44th week of 2022, 322 cases of dengue were reported in Singapore. This brings the total number of cases to 29,894, a 523% increase from the 4,799 dengue cases reported in the same period (Epidemiological Weeks 1 to 44) in 2021 [3,4].

N,N-diethyl-3-methylbenzamide (DEET) is one of the most effective insect chemical repellents [5]. Although it is generally used in insect repellent products, there are some concerns about the effects on children, fetal health, and aquatic organism. There are reports of the symptoms from DEET exposure, it has been shown various effects, including skin reactions, neuropathologies and cardiovascular system [6]. To avoid the harmful effects, plant-derived repellent products, e.g., essential oils, are provided as an alternative [7]. Essential oils are considered as an environmentally friendly and harmless for humans [5]. Chemical compositions that showed mosquito repellent activity, including monoterpenes such as α-pinene, cineole, eugenol, limonene, terpinolene, citronellol, citronellal, camphor, and thymol; sesquiterpenes such as β-caryophyllene; and phytol, linear diterpene alcohol [8]. Several plants e.g., *C. nardus* (citronella grass), *S. aromaticum* (clove), *Z. limonella*, etc. are contained chemical compositions as mentioned above, which *C. nardus, S. aromaticum, and Z. limonella* are mainly contained citronellal, eugenol, and limonene, respectively. For example, the repellent activity of *C. nardus* with 10%, 50%, undiluted concentrations gave 0, 60 and 120 minutes of protection time, respectively, against the yellow fever mosquito (*Ae. Aegypti*). For *S. aromaticum* with 10%, 50%, undiluted concentrations gave 30, 60, and 120 minutes of protection time, respectively, against *Ae. Aegypti*. For *Z. limonella* with 10%, 50%, undiluted concentrations gave 30, 80, and 120 minutes of protection time, respectively, against *Ae. Aegypti*, which can spread dengue fever, chikungunya, yellow fever, and other viruses' diseases [9]. In this study, *Zanthoxylum limonella* (*Z. limonella*) or Ma-khwaen is a selected plant for the essential oil extraction due to the repellent activity and availability in Thailand.

In Thailand, Ma-khwaen's fruits and seeds are widely used as a spice and traditional medicine treatment for dental caries, febrifugal, rheumatism, diuretic, stomachache, and diarrhea [10]. Essential oil from the fruit of Z. *limonella* showed major chemical compositions, which are limonene, terpinene-4-ol and sabinene [11].

The essential oil from *Z. limonella* possesses limonene (43.63%) as a main chemical composition which plays an important role for mosquito repellent and larvicidal activity [11]. There have been reports due to the repellency of essential oil from the fruit of *Z. limonella*, an arm-in-cage test against mosquito species, which are *Ae. aegypti, Culex quinquefasciatus*, and *Anopheles dirus*, these mosquitoes are commonly found in Thailand. The repellency of essential oil gave protection time for 2 hours and for 4-5 hours against *Ae. aegypti* and *Ae. Ablbopictus* mosquitoes, respectively, which *Ae. Ablbopictus* is a vector of dirofilariasis and chikungunya virus [9].

To extract essential oils, there are several methods—steam distillation, ultrasound assisted extraction, water-distillation, etc. For several studies, water distillation or hydro-distillation method were the most used technique for extracting essential oils, this is an inexpensive method as no organic solvents must be presenced [12]. Moreover, this method is one of the oldest methods, which is used to extract oils from plants such as wood and flower petals.

Tan Phat Dao et al, 2020 [13] used hydro-distillation method to extract *Citrus grandis L* Peels essential oil. The results showed that water to solid ratio of 5:1 (mL:g) and temperature 120 ^{o}C at extraction time 113 min, gave highest essential oil content of 1.9% v/w and high in limonene compound compared with the reported supercritical fluid extraction method. Mayura et al, 2022 [14] extracted dried fruit *Z. limonella* at water to solid ratio of 2:1 (mL:g) and rate of distillation was two drops of essential oil per second at extraction time 5-6 h, gave 9.27% v/w essential oil yield.

The kinetics of hydro-distillation have been extensively studied, and it showed the changes in essential oils over time during the hydro-distillation process can be best explained by kinetics that includes both washing and diffusion steps. S Ž Svetomir et al, 2013 [15] studied the kinetics modeling of essential oil extraction from various plant materials by hydro-distillation to find a suitable model. The experimental data for the kinetics of essential oil distillation from juniper berries were obtained from this study, while data for other plants were obtained from experimental results reported in other papers. In addition, data on the kinetics of hydro-distillation of essential oils were collected from several pieces of literature. Three models were the most studied, including a 3-parameter physical model that was developed based on the assumptions of simultaneous washing and diffusion, instantaneous washing followed by diffusion, and diffusion of essential oils only. Mean relative percent deviation (MRPD) to assess the fit of each model. From the results, it was found that the simultaneous washing and diffusion model of essential oils was the best model as the lowest MRPD was 5.5 compared to the model with instantaneous washing followed by diffusion and only diffusion of essential oils resulted in MRPD of 5.9 and 16.7, respectively [15].

The evaluation of physical properties is an important step when simulating essential oil conditioning processes. Therefore, attempts are made to determine thermodynamics relationships that describe the properties required for the calculation of phase equilibrium. L. Mota et al, 2022 [16] conducted thermodynamics and computational modeling studies involving the vapor-liquid equilibrium (VLE) of three of the most common essential oil components in the cosmetic industry: limonene, linalul, and geraniol. The study assessed the non-ideality of the mixture using the

coefficient of activity measured by the modified Raoult's law and examined the use of COSMO-SAC and UNIFAC thermodynamics models to assess the true VLE of fragrance ingredients. The results obtained indicate that the molar fraction of the vapor phase predicted by the UNIFAC and COSMO-SAC models is close to the true value observed in the experiment. Calculations of molar constituents in the vapor phase of mixtures from UNIFAC models offer the possibility to verify the performance of these models. Which is about the behavior of molecules, properties and the ability to interact with molecules.

Thus, the extraction of essential oil from the fruit of *Z. limonella* by hydro-distillation method will be conducted in order to evaluate the optimal conditions by varying water to solid ratio, temperature, and extraction time to obtain maximum yield. In addition, the kinetics model and thermodynamics model will be explored.

1.2 Objectives

1.2.1 To optimize the extraction parameters to enhance yield of the *Z. limonella* essential oil.

1.2.2 To study kinetics model for predicting the amount of *Z. limonella* essential oil extracted.

1.2.3 To study thermodynamics model for prediction of maximum amount of *Z. limonella* essential oil extracted.

1.3 Scopes of Work

1.3.1 Extraction of *Z. limonella* by hydro-distillation
The following important variables will be studied:
- Water to solid ratio (2:1, 3:1, 4:1, 5:1, 6:1, and 7:1 mL/g)
- Extraction time (20-300 min)
- Temperature (130, 140 and 150°C)

1.3.2 Kinetics model for studying a process rate constant (k) and mechanism of the extraction of *Z. limonella*.
The following models will be studied.
- Model of pseudo-first order kinetics.
- Model of instantaneous washing followed by diffusion.
- Model of simultaneous washing and diffusion.

1.3.3 Thermodynamics parameters for studying extraction behavior of *Z. limonella*.

1.3.4 Thermodynamics model will be studied using UNIFAC model and modified Raoult's law.

1.4 Expected Outputs

1.4.1 To obtain maximum yield of essential oil using optimized condition.

1.4.2 Mathematical model for predicting the extracted essential oil content.

1.4.3 Thermodynamics parameters for describing the extraction behavior.

1.4.4 Thermodynamics model for predicting the concentration of important active components.

CHAPTER II

THEORY AND LITERATURE REVIEW

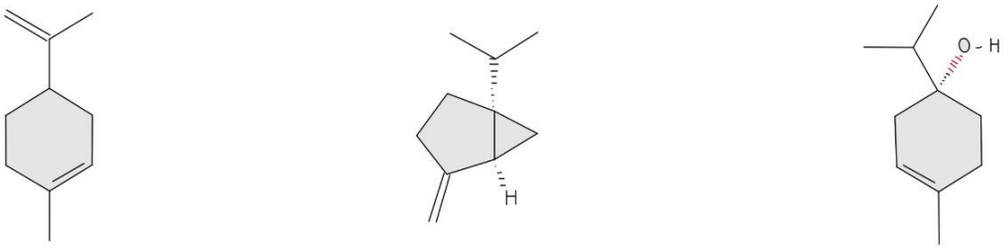
Zanthoxylum limonella (*Z. limonella*) or Ma-khwaen, belongs to the family *Rutaceae,* and is a perennial, aromatic tree with a height of 5-10 meters, *Z. limonella* can be found in Northern Thailand, India, Sri Lanka Myanmar, Indochina, and Papua New Guinea. In Thailand, *Z. limonella* is traditionally used as a spice due to its strong aroma. Most often, the part of *Z. limonella* fruit is mainly used for food, traditional medicine for dental caries treatment, etc. [11].

2.1 *Zanthoxylum limonella*

Figure 2.1 showed the structure of *Z. limonella* fruit which consists of 1) fruit wall, 2) oil gland, 3) mesocarp, 4) endocarp, 5) parenchyma, 6) testa, 7) endosperm [10].

Figure 2.1 Transverse section of *Z. limonella* fruit and seed [10]

R. Supabphol and J. Tangjitjareonkun, 2014 [11] investigated the chemical constituents that were analyzed by gas chromatography-mass spectrometer (GC-MS). The volatile oil of *Z. limonella* fruit consists of approximately 22 compounds and three main volatile oil compounds, limonene (31.09%), terpinen-4-ol (13.94%), and sabinene (9.13%) which is similar to C. Rawiwan, et al., 2016 [10], the research reports the three major volatile oil compounds including limonene (43.63%), sabinene (16.72%), and terpinen-4-ol (10.95%). The structure of these main chemicals is illustrated in figure 2.2.



a) b) c)

Figure 2.2 The major chemical structure of volatile compounds of *Z. limonella* fruits; a) limonene, b) sabinene, c) terpinen-4-ol [11]

Y. Trongtokit et al, 2005 [9] characterized the relationship between different concentrations of 38 selected essential oils against *Aedes aegypti*, *Culex quinquefasciatus* which transmit dengue virus and *Anopheles dirus* which transmit the malaria. The essential oils from *C. nardus* (Citronella grass), *P. cablin* (Patchouli), *S. aromaticum* (Clove) and *Z. limonella* (fruit) were the most effective and provided at least 2 h of *Ae. aegypti* repelling efficiency. Based on these results, *C. nardus, P. cablin, S. aromaticum* and *Z. limonella* (fruit) were further studied for efficacy against two other mosquito species, *Cx. quinquefasciatus* and *An. dirus*, compared to *Ae. aegypti*. Results are shown in Table 2.1, the undiluted oil showed the maximum protection time in each case. As for *Z. limonella*, some species of this genus are insecticidal, the plant produced an essential oil yield of 12.5% (w/w), which is higher than other plants studied such as *C. nardus* and *P. cablin* essential oils which yielded only 1.82% (w/w) and 2.72% (w/w), respectively. So, this makes *Z. limonella* more cost-effective.

Table 2.1 Repellent activity of the promising essential oils against *Ae. aegypti*, *Cx quinquefasciatus* and *An. dirus* mosquitoes [9].

Essential oils	Complete mosquito repellent time (min)			
	Ae. aegypti	*Cx. quinquefasciatus*	*An. dirus*	Control[A]
C. nardus	120	100	70	0
P. cablin	120	150	170	0
Z. limonella	120	170	190	0
S. aromaticum	120	240	210	0

[A] In all cases, each mosquito species caused more than two bites on the untreated control arm prior to the test arm treatment. Duration of complete expulsion recorded by three volunteers: (with the average of all three)

2.2 Essential oil extraction

Essential oil (EO) or volatile oil is an organic substance naturally produced by plants and stored in various parts such as leaves, petals, fruit surfaces, stamens, roots, or the bark of the stem. EO is a liquid with a complex and different chemical

composition, which causes the differences in its odor and properties. EO possesses several properties, such as antimicrobial, anti-inflammatory, anticarcinogenic, inhibitor, and analgesic properties. Because of that, EO tends to be used in many applications—aromatherapy, food industry, insecticide, and medicine [17].

There are several methods used to extract the essential oil, e.g., solvent extraction, steam distillation, supercritical fluid extraction, ultrasound-assisted extraction, and hydro-distillation.

2.2.1 Solvent extraction

The method to extract essential oil by using a volatile solvent such as ethanol, benzene, or hexane to isolate the oils. During this method, the plant material is placed into a solvent bath. After the extraction, the liquid mixture consisting of essential oil along with the other compounds goes through a filtration process and then, a distillation process. The advantage of this method is the low temperature used during the process. However, essential oil production contains a small amount of solvent, which is impossible to use in the food industry [18].

X. Zhang et al., 2012 [19] extracted the essential oil from discarded tobacco leaves at temperature range 30-60 °C by solvent extraction, using petroleum ether, diethyl ether, dichloromethane, and n-hexane. The results indicate the most effective extraction solvent is petroleum ether, the extraction yield is 3.25 ± 0.107% (w/w). At the optimum extraction temperature of 40 °C.

2.2.2 Stream distillation

Stream distillation is applied for the extraction of essential oils by steam passing through the plant material, a tiny pocket that holds essential oil will open and release the essential oil without damaging the oil structure. This method is commonly applied to fresh raw materials that easily decompose due to high temperatures. Because the method temperature could be controlled, it could be conducted below the decomposition temperature of the compounds. On the other hand, because of the low pressure of rising steam, more time is consumed [20].

F. Teshale et al., 2022 [21] conducted the extraction of essential oil from rosemary leaves using steam distillation process. A central composite design (CCD) is applied to evaluate three independent variables such as extraction temperature (103-118 °C), time (2-6 h) and feed mass (200-600 g). The optimum conditions to obtain maximum yield are an extraction time of 4 h, extraction temperature of 113 °C, and feed mass of 500g. The maximum yield is 2.82% (w/w).

2.2.3 Supercritical fluid extraction (SFE)

This method can be operated at near-ambient temperatures for specific solvents. Among the SFE solvents, carbon dioxide (CO_2) is the most widely used solvent. Due to CO_2 properties, including non-flammability, non-toxicity, and lack of residue in the final product. SFE provides valuable ingredients from

herbs with high yield and good quality. However, the main obstacle to this method is the cost of the equipment compared with other methods [20].

M. Shrigod et al., 2016 [22] studied to optimize the process of supercritical fluid extraction of essential oil from mint leaves (*mentha spicata*) using central composite design. The effects of temperature (35–55 °C), pressure (100–300 bar), dynamic time (20–90 min), and particle size (0.2–1.0 mm) were evaluated to essential oil yield. The optimum process parameters obtained from numerical optimization are dynamic time of 37.5 min, extraction temperature of 48 °C, pressure of 151 bar, and particle size of 0.40 mm. The yield of essential oil is 1.4% (w/w).

2.2.4 Ultrasound-assisted extraction (UAE)

In UAE, the effects of ultrasound are due to the breakdown of microscopic bubbles and the phenomena of cavitation. After the bubbles increased the size, they collapsed violently. Due to the violent collapse, the mechanical forces increased, which led to cell membrane damage, resulting in a high yield of extraction and less time consumed. Nevertheless, this method is expensive in capital cost [18].

K. Tekin et al., 2015 [23] investigated the optimization of UAE process parameters of essential oils from clove using central composite design (CCD). The parameters were optimized by using response surface methodology (RSM). Three variables were extraction temperature range from 32 to 52 °C, extraction time range from 30 to 60 min, and plant concentration range from 3% to 7%. The result showed the optimum extraction parameters in an ultrasound with a frequency of 53 kHz, including extraction time is 45 min, extraction temperature is 42 °C, and concentration is 5% which the extract yield is 23.95% (w/w).

2.2.5 Hydro-distillation

This method use water as solvent, the mechanism for hydro-distillation extraction is similar to that of Soxhlet extraction process. In this method, the sample and water solvent are placed and heated in the heater. The hot water causes small sacs in plant material which contain essential oil to burst. The extracted oil is then transported by steam in vapor phase into the condenser then the liquid mixture is formed. The liquid mixture is flowed into separator where essential oil and water can be separated by their density difference. In addition, the temperature in this method must be strictly observed to prevent thermal compound degradation such as the degradation of limonene can be composed above 450 °C [24]. The main advantage of hydro-distillation is that it does not require expensive solvent. However, the overall process requires a long period of time [20].

H. Cui et al., 2018 [25] conducted the optimization of hydro-distillation extraction of essential oils from *Carex meyeriana* Kunth by RSM. Three variables were optimized by RSM, including ratio of liquid to solid range of 10:1 to 50:1 mL/g, extraction time range of 3 to 11 h, and particle size range of 10 to 40 mesh. The optimal conditions for the essential oils were estimated:

liquid/ solid ratio at 43:1, extraction time of 9 h, and particle size of 10 mesh. The actual yield was 0.13% (w/w).

T.B.Y. Nguyen et al. 2022 [26] extracted essential oil from the leaves of *M. balansae* using hydro-distillation. They tested different water to solid ratios ranging from 1:1 to 6:1 mL/g and distillation times of 30-150 minutes. The optimum conditions were found to be a water to solid ratio of 4:1 mL/g and a distillation time of 120 minutes, resulting in the highest essential oil yield of 1.33%.

D.T. Phat et al. 2022 [27] extracted essential oil from *Citrus microcarpa* using the Clevenger tool (Figure 2.3) and the hydro-distillation process. They optimized the extraction process by varying the water to solid ratio 2:1, 3:1, and 4:1 mL/g and heating capacity 170, 204 and 238 W. It was found that the maximum essential oil content of 4.2% (v/w) was obtained through water distillation under extraction conditions as a water to material ratio of 3:1 mL/g, a heating power of 204 W, and an extraction time of 60 min. In addition, the chemical composition of the essential oil was analyzed using GC-MS, and it was found that limonene 88.64% was the main constituent.

E. Lainez-Ceron et al. 2019 [28] performed hydro-distillation of eucalyptus essential oil. The different process variables including water to solid ratio (1:1, 3:1, or 5:1 mL/g) and stirring speeds (0, 200, or 400 rpm) were optimized. The maximum yield obtained is 1.19% (w/w) by using the system with a water to solid ratio of 5:1 mL/g and using a stirring speed of 400 rpm.

M. Madhumita et al. 2019 [29] optimized the extraction parameters by the Box-Behnken design of response surface methodology of fresh and cured betel leaf essential oil. The hydro-distillation method was performed using Clevenger type apparatus that heated by a heating mantle. In this study, three independent variables such as extraction time (40-140 min), temperature (80-100 °C), and water to solid ratio (1:1-2:1 l/g) were optimized to get a maximum yield. The optimal conditions of extraction time (140 min), extraction temperature (100 °C), and water to solid ratio (1.5:1 l/g), and the maximum yield obtained is 0.35% (v/w) and 0.48% (v/w) of fresh and cured betel leaf essential oil.

The previous research studied the hydro-distillation report the important of water to solid ratio, temperature, and time to the yield of essential oil as show in Table 2.2

Table 2.2 The optimal condition of essential oil extraction from various methods.

Plants	Method	Water to solid ratio	Temperature	Time (hour)	Yield	Ref.
Lemon peels	Hydro-distillation	3:1 mL/g	130 °C	1.60	0.021 mL/g	[30]
Peppermint leaves	Hydro-distillation	1:6 mL/g	130 °C	2.00	0.051 mL/g	[31]
	microwave assisted extraction	1:2 mL/g	540 W	0.30	0.082 mL/g	
Pomelo peels	Hydro-distillation	1:5.07 mL/g	120 °C	1.89	0.045 mL/g	[32]
Jasmine	Hydro-distillation	1:5 mL/g	120 °C	6.00	0.092%	[33]
Pomelo peels	Hydro-distillation	1:5 mL/g	120 °C	1.75	0.019 mL/g	[34]
Thlaspi arvense L. leaves	Microwave-assisted hydro-distillation	1:10 mL/g	624 W	0.57	0.770 mg/g	[35]
Thlaspi arvense L. seeds	Microwave-assisted hydro-distillation	1:10 mL/g	624 W	0.57	2.690 mg/g	

2.3 Kinetics model

2.3.1 Model of pseudo-first order kinetics

S.B. Santos et al, 2015 [36] used the diffusion model to describe mass transfer as a solution to Fick's second law. However, mass flow by diffusion requires knowledge of intra-particle concentration gradients, which is uncertain to specify at the solid-liquid interface. The mass flow by diffusion is equal to the mass flow by convection, given that the process takes place under unsteady conditions and without chemical reactions. The rate of change of oil concentration in the liquid phase can be expressed as follows:

$$\frac{dq_L}{dt} = k(q_{Le} - q_L) \quad (1)$$

where q_L and q_{Le} are the oil concentrations ($g.L^{-1}$) in the liquid phase at time t (min) and at equilibrium, respectively, and k is the process rate constant (min^{-1}) in solution. Equation (1) is subject to the following initial conditions:

(i) At the start of the extraction process (t = 0), the oil concentration in the liquid phase is assumed to be zero (q_L = 0).

The integration of (1) considering the given conditions results in:

$$q_L = q_{Le}(1 - \exp(-kt)) \quad (2)$$

2.3.2 Model of simultaneous washing and diffusion

S Ž Svetomir et al, 2013 [15] investigated the hydro-distillation kinetics of juniper essential oil and literary data on the hydro-distillation kinetics of essential oils from various plant materials. A three-parameter physical model was developed using the simultaneous washing and diffusing process of essential oil.

The mathematical model is based on the following assumptions:

a) the suspension in the distillation vessel is perfectly mixed.

b) the essential oil is considered as a single component.

c) plant particles are isotropic, equal in size, shape, and initial essential oil content.

d) the effective coefficient of diffusion through plant particles is constant.

e) there is no resistance to the mass transfer of essential oil from the external surfaces of the plant particles.

f) the essential oil and the floral water are completely immiscible.

g) a fraction of the essential oil is located at the external surfaces of the plant particles, f, and the rest is uniformly distributed in the plant particles, (1-f).

h) the isolation of essential oil occurs via two simultaneous mechanisms: 1) "washing" of the essential oil from the external surfaces of the plant particles

and 2) the “diffusion” of essential oil from the interior of the plant particles towards their external surfaces. The kinetics of both processes is assumed to be the first order with respect to the essential oil in the plant particles.

$$-\frac{dq_p}{dt} = kq_p \tag{3}$$

where q_p is the average concentration of essential oil in the plant particles at time (g/30 g)

k is the process rate constant (min^{-1})

t is time (s)

The washing and diffusional process has a different rate constant: the diffusional process is much slower than the washing and is responsible for limiting the overall extraction process rate.

i) The amount of essential oil available for hydro-distillation corresponds to the amount of saturated essential oil.

$$q_{po} = q_\infty \tag{4}$$

where q_{po} is the initial average concentration of essential oil in the plant particles (g/30 g of the plant materials)

q_∞ is the amount of essential oil distilled off until saturation (g/30 g of the plant materials)

By integrating Equations (3), the following equations are derived for washing and diffusion, respectively:

$$\frac{q_{p1}}{q_\infty} = e^{-k_1 t} \tag{5}$$

and:

$$\frac{q_{p2}}{q_\infty} = e^{-k_2 t} \tag{6}$$

where k_1 is the rate constants for washing processes (min^{-1})

k_2 is the rate constants for diffusion processes (min^{-1})

Based on the assumption g), the total amount of essential oil remained in the plant particles until time t is as follows:

$$\frac{q_p}{q_\infty} = f\frac{q_{p1}}{q_\infty} + (1-f)\frac{q_{p2}}{q_\infty} \tag{7}$$

or:

$$\frac{q_p}{q_\infty} = fe^{-k_1 t} + (1-f)e^{-k_2 t} \tag{8}$$

where f is the fraction of the essential oil located at the external surfaces of the plant particles

The amount of essential oil recovered until time *t*, q is connected to the amount of the essential oil present in the plant particles at the same time by the following equation:

$$q = q_{\infty} - q_p \tag{9}$$

By combining Equations (8) and (9), the following equation is derived:

$$\frac{q}{q_{\infty}} = 1 - fe^{-k_1 t} - (1 - f)e^{-k_2 t} \tag{10}$$

2.3.3 Model of instantaneous washing followed by diffusion

This model, assuming rapid and instantaneous washing, assigns ($k_1 \rightarrow \infty$), so equation (10) becomes:

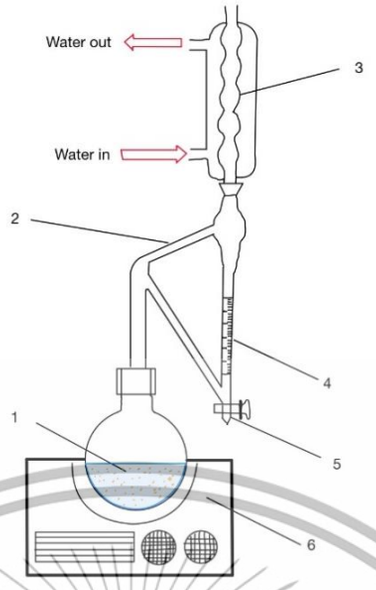
$$\frac{q}{q_{\infty}} = 1 - (1 - f)e^{-k_2 t} \tag{11}$$

The equation can be simplified by setting f = 0 (without essential oil washing), resulting in a pseudo-first order kinetics equation (2).

2.4 Hydro-distillation process

Hydro-distillation is a traditional method of extracting bioactive compounds, mainly essential oils from plants [26,27]. Hydro-distillation involves three main physicochemical processes: hydro-diffusing, hydrolysis, and thermal decomposition [39].

In this method, the plant material is placed in a still chamber, then a sufficient amount of water is added and brought to a boil, or steam may be injected directly into the plant sample. The mixture of water vapor and oil is condensed by indirect cooling with water. The condensed mixture flows from the condenser to the separator. where oil and bioactive compounds are automatically separated from water as show in figure 2.3 [40].



(1) round-bottom flask; (2) fractioning column; (3) vapor condenser; (4) scaled capillary for volume measurement; (5) stopcock; (6) electric heater with a thermal control unit

Figure 2.3 The schematic apparatus for hydro-distillation or Clevenger apparatus

During hydro-distillation, an increase in temperature causes an increase in the pressure inside the plant organs containing essential oils. When the pressure rises above a certain level, the cell wall is ruptured, and essential oils are released. Part of the essential oil is released from the external surface of the plant particles. But the rest must be diffuse from the inside of the plant particles to the external surface. The steam then removes the essential oil from the external surface of the plant particles [15].

From the hydro-distillation mechanism of extraction. The main process parameters are the water to solid ratio, temperature, and extraction time.

2.4.1 Water to solid ratio

Determining the ratio of water to solid is essential for the extraction process during boiling distillation, the essential oils in the plant cells diffuse to the surface of the material and are carried by steam. At the same time, water penetrates the material in the opposite direction, and the oil will continue to be blown into the water. This process takes place until the essential oils in the tissues are completely removed. Therefore, the determination of the water to solid ratio is necessary for the extraction process to achieve maximum yield. By extracting pomelo peels, the water to solid ratio with the highest yield is 5:1 mL/g. In the low water ratio of 2:1 to 3:1 mL/g, the low amounts of essential oils collected were caused by insufficient water to dissolve the colloidal wrap around essential oil bag, this leaves a large amount of residual essential oil in the material. Conversely, at higher ratios, such as 6:1 to 7:1 mL/g, the amount of essential oil received was not high. This is due to the slow evaporation rate and the loss of oil in the storage pipe [34].

T H Tran et al, 2021 [30] studied the extraction of lemon peels essential oil using hydro-distillation method. The variables studied were water to solid ratio (1.32 to 4.68 mL/g), extraction temperature (103 to 137 °C) and extraction time (0.66 to 2.34 h) to be optimized by response surface methodology. According to the results, the optimum condition was water to solid ratio 3:1 mL/g at 120 °C for 1.6 hour. The highest essential oil yield was 2.097% (v/w). The main compound found in lemon essential oil is limonene compound, which accounts for 66%.

T Bui-Phuc et al, 2020 [31] evaluated the parameters related to the extraction of essential oils from peppermint leaves by hydro-distillation (at temperature 130 °C) and microwave assisted extraction, which has involving mint leaf drying periods (30, 60, and 90 mins) at 50 °C, water to solid ratios (4:1, 6:1, 8:1, and 10:1 for hydro-distillation and 1:1, 1.5:1, 2:1, and 2.5:1 for microwave assisted extraction), extraction durations (60-180 for hydro-distillation and 10-25 mins for microwave assisted extraction), and microwave energy (230, 380, 540, and 700 W), the chemical composition of essential oils obtained from hydro-distillation and microwave assisted extraction were compare. At 50 °C the drying time of 60 min gave to approximately 40% moisture, showing maximum yield for hydro-distillation and microwave assisted extraction, and the optimal extraction conditions were: water to solid ratio 6:1 (mL/g), 120 min extraction time at 130 °C for hydro-distillation with yield of 0.0510 mL/g. When using microwave assisted extraction, the optimum condition was 1:2 material to water ratio (mL/g), 20 min extraction time and 540 W microwave power for microwave assisted extraction with yield of 0.0832 mL/g. However, D-limonene content from hydro-distillation extraction yielded higher than microwave assisted extraction, 1.4% (w/w) and 0.3% (w/w), respectively.

T P Dao et al, 2020 [32] investigated the relationship between hydro-distillation parameters on the efficiency of the essential oil recovery process from Vietnamese grapefruit (*Citrus grandis L.*) peels by studying the water to solid ratio parameter (3.32:1 to 6.68:1 mL/g), extraction temperature (103.18 to 136.82 °C) and extraction time (79.77 to 130.23 min). The central composite design (CCD) was used in the design of the experiment. As a result, the optimum parameter was water to solid ratio of 5.07:1 mL/g, temperature at 119.29 ºC and extraction time of 113.68 min, gave a maximum yield of 4.46 % (v/w). D-limonene was found to be the main component (97.318 %) of essential oils.

Z. Gu et al., 2021 [41] studied to identify and analyze the factors to maximize the yield of rosemary essential oils and reduce the cost by hydro-distillation method. Single-factor experiments are then used the first-order kinetics to verify the data. The parameters were varied to optimize, which are ratio of water to solid range of 1:1 to 1:3 (mL/g), concentration of NaCl range of 1.5% to 5%, and leaf and branch integrity of the current year range from 1-cm pieces to 2-cm pieces. The results showed a 1:3 mL/g of water to solid ratio, 2-cm pieces and 3 h with NaCl concentration at 5% gave the high extraction yield 2.67% (w/w).

R. Zhao et al., 2022 [35] developed the microwave-assisted hydro-distillation to obtain the maximum yield from *Thlaspi arvense L.* leaves (TAL) and seeds (TAS). Three operational parameters including water to solid ratio (7.5, 10.0, 12.5 mL/g), microwave irradiation power (385, 540, 700 W) and microwave irradiation time (20, 30, 40 min) were optimized by Box-Benhken design. The results showed the optimum condition are a water to solid ratio of 10 mL/g, microwave irradiation power of 624 W and microwave irradiation time of 34 min. For the maximum yield of TAL and TAS were 0.77 mg/g and 2.69 mg/g, respectively.

2.4.2 Temperature

The extraction temperature is an important parameter that affects the quality of essential oils since the hydro-distillation method must be extracted at a temperature of more than 100 °C because of the boiling point of water. At high extraction temperatures, some volatile components may be lost [42]. In this study, we focused on an active component which is limonene and another study reported about the degradation temperature showed that it will degrade at 450°C. However, high temperatures are required in this process to break up hydrogen bonds in water. This results in the decreasing of dielectric constant, so water can be dissolved in the essential oil [43].

D T Phat et al, 2020 [13] studied of hydro-distillation extraction parameters to optimize for maximum pomelo (*Citrus grandis L.*) peel essential oil, with parameters size of material (original, cut fiber and grind), water to solid ratio (2:1 to 7:1 mL/g), extraction temperature (100 to 140 °C) and extraction time (60 to 135 min). The results showed that the optimum conditions were material size grind, water to material ratio 5:1 mL/g, extraction temperature 120°C and extraction time 105 min, yielding the highest essential oil yield of 1.9% (v/w) with limonene as the main constituent 97%. The heat and steam generated at 120 °C cause more severe ruptures on the plant cells, therefore highlighting the pushing of essential oils to the surrounding medium. Therefore, a temperature of 120°C was considered optimal for pomelo peel by water distillation. This is because temperatures above this threshold can cause essential oils to decompose.

N D Phuc et al, 2019 [33] determined conditions during hydro-distillation to optimize jasmine extract. The parameters studied were extraction time (4 to 8 hour), extraction temperature (110 to 150 °C), raw material size (grind fresh, fresh and dry grind) and water to solid ratio (1:1 to 5:1 mL/g). The results showed that at 6 hours, 120 °C, grind fresh and ratio of 2:1 (mL/g) are optimal parameters and maximum yield of 0.092% (w/w).

2.4.3 Extraction time

Extraction time is also an important parameter in the extraction of essential oils from plants. The essential oil extraction time depends on the temperature used for extraction. In general, the longer the extraction period, the solvent has longer contact with the plant cells and then to completely extract the essential oils from the plant matrix. Optimizing the extraction time not only influences oil yield but also saves time and energy for the entire refining process. To extract essential oil from Japanese mint, the optimum extraction time was 60-120 min, depending on the extraction temperature [31].

2.5 Thermodynamics Parameters

Thermodynamics parameter including enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) for extraction of *Z. limonella* essential oil can be estimated using Van't Hoff equation (12):

$$\ln K = \frac{-\Delta H^\circ}{R}\frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (12)$$

where K is the equilibrium constant of extraction process, R is gas constant, T (K) is absolute temperature of extraction process, ΔH° (KJ mol^{-1}) is extraction enthalpy and ΔS° (J mol^{-1} K^{-1}) is extraction entropy.

The equilibrium constant (K) was determined using the following equation (13):

$$K = \frac{C_{Le}}{C_{Se}} = \frac{Y_{Le}}{Y_{Se}} \quad (13)$$

where C_{Se} is the oil concentration in the solid phase at equilibrium (gL^{-1}), C_{Le} is the oil concentration (gL^{-1}) in the liquid phase at time t (min) and at equilibrium, respectively, Y_{Se} is the percentage of oil not extracted at equilibrium, obtained by mass balance, and Y_{Le} is the percentage of oil contained in the liquid phase at equilibrium in relation to the oil contained in the sample at time t=0.

The variations in Gibbs free energy (ΔG°) for the different temperatures were estimated by the equation (14):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

where ΔG° (KJ mol^{-1}) is Gibbs free energy. In addition, graphs were generated via the data ln K versus 1/T which enthalpy and entropy can be calculated [38,39].

2.6 Prediction of the concentration of important active components by thermodynamics equation

2.6.1 Phase equilibrium

R.N. Almeida et al. 2017 [45], the equilibrium phase was calculated using modified Raoult's law at low pressure without sacrificing accuracy, as the vapor phase behaves as an ideal gas and the non-ideality effect on the liquid phase is considered through the activity coefficient.

$$y_i P = x_i \gamma_i P_i^{sat} \quad (15)$$

Where P is the system pressure, y_i and x_i are the molar fractions in the vapor and liquid phases, respectively, P_i^{sat} is the vapor pressure of pure substances, and γ_i is the activity coefficient of component i in a mixture.

2.6.2 Vapor pressure

Vapor pressure (P_i^{sat}) is a crucial physicochemical property in chemical engineering process design. It represents the external pressure required for the extracted system to remain in thermodynamics equilibrium at a specified temperature and is the pressure exerted by the vapor of a given element when in thermodynamics equilibrium. It can be expressed as a measure of the vaporization tendency of pure substances or as a measure of volatility in the case of vapor-liquid mixtures, such that the rates of vaporization and condensation are equal [46]. Antoine equation eqn. (16) is used to calculate the vapor pressure of the individual components of the mixture.

$$log_{10} P^{sat}(mmHg) = A - \frac{B}{T(℃)+C} \quad (16)$$

2.6.3 UNIFAC Model

The UNIFAC model is widely used for calculating interactions in mixtures, showing positive or negative deviations from Raoult's law. It serves as a basis for other models, allowing the residual and combinatorial terms to be modified, and new functional groups to be added to achieve better results after studying the solution [46]. In this model, the activity coefficients were determined in terms of contributors and residuals using the following equations:

$$ln\gamma_i = ln\gamma_i^{comb} + ln\gamma_i^{res} \quad (17)$$

The combinatorial part ($ln\gamma_i^{comb}$) accounts for differences in the size and shape of molecules (contribution of excess entropy), while the residual part ($ln\gamma_i^{res}$) mainly accounts for the effects of energetic interactions between groups (contribution of excess enthalpy).

Contributions to the UNIFAC model take into account the shape and size of molecules in a mixture [47].

$$ln\gamma_i^{comb} = 1 - J_i + lnJ_i - 5q_i(\ln\frac{\emptyset_i}{\theta_i} + 1 - \frac{\emptyset_i}{\theta_i}) \quad (18)$$

where the quantity J_i, is given by.

$$J_i = \frac{\emptyset_i}{x_i} \quad (19)$$

The molecule volume fraction $\emptyset_i$ and the molecule surface area fraction θ_i are given by eqn. (20) and eqn. (21).

$$\emptyset_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (20)$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \tag{21}$$

The first three terms in Equation (18) correspond to the Flory-Huggins expression, while the last term is the Staverman-Guggenheim correction term. Equations (20) and (21) provide the relative molecular volume (r_i) and the relative molecular surface area (q_i), respectively.

By

$$r_i = \sum_k v_k^{(i)} R_k \tag{22}$$

$$q_i = \sum_k v_k^{(i)} Q_k \tag{23}$$

In equations (22) and (23), the parameter $v_k^{(i)}$ represents the number of k-type subgroups in the molecules of species i. The relative molecular volume r_i and relative molecular surface area q_i are then calculated using the subgroup parameters R_k and Q_k. The values for R_k and Q_k were obtained from Y.V.C. Rao's 1997 [48].

Basically, the combinatorial part represents the excess entropy of mixing due to differences in shape and size, while the remainder represents the excess enthalpy of mixing as a result of different interaction energies. The residual part of the UNIFAC model takes into account the energetic interactions between different groups. Inter-molecular interactions can be calculated from the group activity coefficients in both mixtures and pure substances.

$$ln\gamma_i^{res} = \sum_k v_k^{(i)} (ln\Gamma_k - \Gamma_k^{(i)}) \tag{24}$$

where Γ_k is the group activity coefficient of group $\Gamma_k^{(i)}$ in the mixture and is the group activity coefficient of group k in pure substance i at the same conditions. The group activity coefficient Γ_k was calculated according to:

$$ln\Gamma_k = Q_k[1 - \ln(\sum_m \Theta_m \Psi_{mk})] - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \tag{25}$$

where Θ_m is the area fraction of group m, and the sum is above all groups. Θ_m is calculated in a similar way to θ_i in the combinatorial part, according to

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{26}$$

where X_m, is the mole fraction of group m in the mixture.

$$X_m = \frac{\sum_j v_k^{(i)} x_j}{\sum_j \sum_n v_k^{(i)} x_j} \tag{27}$$

In equation (25), the group interaction parameter Ψ_{nm} is a temperature dependent parameter and is given by

$$\Psi_{nm} = \exp\left(-\frac{a_{nm}}{T}\right) \quad (28)$$

where a_{nm} is a measure of the interaction energy between n and m groups and is considered independent of temperature. Group interaction parameters a_{nm} (Units of degrees Kelvin) are obtained from Y.V.C. Rao's 1997 [48]. UNIFAC, however, has the following limitations.

1. The UNIFAC method does not distinguish between isomers.
2. Since it is based on a $\gamma - \phi$ (i.e., combined method) approach, its application is limited to moderate pressures, depending on the equation of state selected and on the influence of pressure on γ_i.
3. Temperatures are limited to the approximate range of 2-150°C.
4. Non-condensable gases, polymers, and electrolytes are excluded.
5. UNIFAC parameters based on VLE data cannot be used for LLE predictions.
6. "Proximity" effects are not accounted for; for example, --CH groups in alcohols and glycols do not have the same effect.

CHAPTER III

RESEARCH METHODOLOGY

3.1 *Z. limonella* preparation

The dried fruits of *Z. limonella* were purchased from Chiang Mai province, northern Thailand. The raw material was blended by using kitchen blender to increase the surface area and then sieve to 600-850 μm [15]. The dried fruits of *Z. limonella* powder were stored in a box at room temperature for further extraction.

3.1.1 Apparatus

- Kitchen blender
- Sieve shaker in range 600-850 μm

3.1.2 Procedures

- Grind the dried fruit of *Z. limonella* with kitchen blender around 5 sec
- Sieve the fine dried fruits of *Z. limonella* to 600-850 μm
- Stored in a box at room temperature

3.2 Hydro-distillation

In this study, three parameters including water to solid ratio, extraction temperature, and extraction time were investigated.

3.2.1 Apparatus

- Beaker
- Round bottom flask 250 mL
- Fractional column
- Vapor condenser
- Stopwatch
- Thermocouple
- Hotplate stirrer
- Silicone tube
- Clamp holder and metal support stand

3.2.2 Solvent

- *Z. limonella* powder
- Deionized water

3.2.3 Procedures

1. Weigh 30 g of *Z. limonella* powder and mix with 60, 90, 120, 150, 180 and 210 mL of deionized water (2:1, 3:1, 4:1, 5:1, 6:1 and 7:1 mL/g), each ratio for one set of experiment, then put in the round bottom flask.

2. Heating through an oil bath, using thermocouple to control the temperature, at specified value of 130, 140 and 150 °C for specified time (20-300 min).

3. After specified extraction condition, the liquid mixture flows into a separator where water and the essential oil are separated by gravity caused of

density difference, then put the extraction liquid in measuring cylinder glass to measure the volume of essential oil.

4. The experiment was run in triplicate for each water to solid ratio at a temperature of 150°C and an extraction time of 60 minutes. This was done to evaluate the effect of different water to solid ratios on the outcome of the experiment.

5. The experiment was run in triplicate at temperatures of 130°C, 140°C, and 150°C, with extraction times ranging from 20 to 300 minutes, using a water to solid ratio of 5:1 mL/g. The purpose of this was to assess the impact of varying temperature and extraction time on the experimental results and to determine a suitable kinetics model for the system.

6. After measure the volume of essential oil, calculate the yield by [30–33]

$$\text{Yield \% (v/w)} = \frac{\text{Volume of essential oil (mL)}}{\text{Weight of } Z.\ limonella \text{ powder (g)}} \times 100 \quad (11)$$

7. The yields % (v/w) at a water to solid ratio of 5:1 mL/g for temperatures of 130°C, 140°C, and 150°C, within the specified time range of 20-300 minutes, were multiplied by the density of *Z. limonella* essential oil, which is 0.853 g/mL, in order to convert them to weight/weight yields % (w/w).

8. fit the values into three kinetic equations: Pseudo-first kinetic model Simultaneous washing and diffusion model and washing immediately followed by a diffusion model to find a suitable model

3.3 Prediction of the concentration of important active components

A modified Raoult's law equation (15) was employed to determine the concentrations of important active components including limonene, sabinene, and other (alpha-pinene) in *Z. limonella* essential oil for vapor-liquid equilibrium (VLE) at temperatures of 130, 140, and 150°C. To calculate the activity coefficient for VLE prediction, the UNIFAC model equation (17-28) was utilized. The liquid fraction was determined through a trial-and-error process, where the sum of the liquid fugacity of each individual compound was divided by the sum of the individual vapor fractions, resulting in an equality with atmospheric pressure or 760 mmHg.

3.4 Chemical composition analysis by GC-MS

The chemical composition of *Z. limonella* essential oil was analyzed by gas chromatography-mass spectrometry at the school of science, King Mongkut's Institute of Technology Ladkrabang using a GC-MS apparatus (GC 6890-N, MS, Agilent Technologies 5973) with an Agilent J&W HP-5 column (30 m × 0.25 mm id) and a film thickness of 0.25 μm. A sample of 0.2 μl was injected into the helium (99.99%) column as a phase, which was oscillating and flowing at a rate of 1 mL/min. The column oven temperature was initially set at 50 °C (held for 3 min) and then increased by 10 °C per minute to 200 °C (held for 2 min) and further increased by 10 °C per minute to 270 °C (held for 15 min). All chemical constituents were identified using Agilent software (Version G1701DA D.00.00). The identity of each chemical identified by GC-MS was confirmed by Sequestration Index Comparison.

CHAPTER IV

RESULTS AND DISCUSSION

The process variables, which are water to solid ratio, extraction temperature, and extraction time were investigated to find the optimum conditions for essential oil extraction from the powder of *Z. limonella* fruits by using hydro-distillation process. After optimizing all variables, the relationship of obtained data including extraction temperature and extraction time will be used into kinetics models in order to determine process rate constant (k). In addition, the thermodynamics model will be studied to find the maximum component in essential oil at different temperature.

4.1 Factors affecting essential oils from *Z. limonella* extraction.

4.1.1 Effect of water to solid ratio

The powder of *Z. limonella* fruit was mixed with water at different ratio, then extracted through hydro-distillation extraction process with extraction temperature of 150 °C for 1 h. We chose an extraction temperature of 150°C because it represents the highest temperature range studied. At higher temperatures, the dielectric constant of water decreases, leading to increased solubility of water in the essential oil [33, 43].

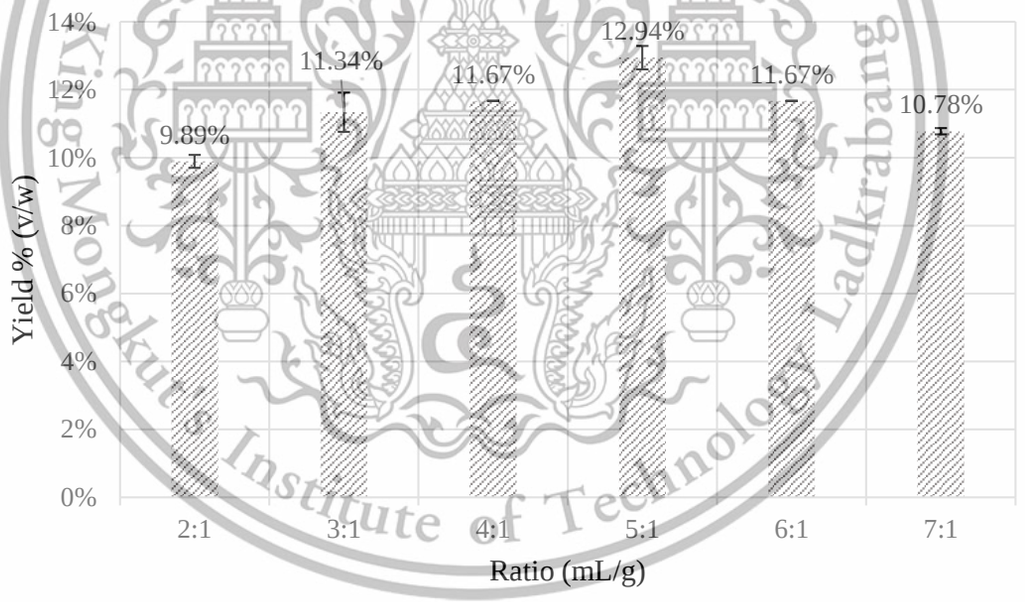


Figure 4.1 Effect of water to solid to the yields of essential oils at temperature of 150 °C for an extraction time of 1h.

Figure 4.1 showed the effect of water to solid ratio, where the yields of 2:1 (9.89 ± 0.19%v/w), 3:1 (11.34 ± 0.58%v/w), 4:1 (11.67 ± 0.00%v/w), and 5:1 (12.11 ± 0.34%v/w) mL/g ratio showed ascending trend, as the results, showed that low in water to solid ratio, the lower yields occur, due to the insufficient water to dissolve essential oil. When adding more water to extract, the higher oil content was obtained due to the increasing of water where large amount of water improve the ability to dissolve the colloidal wrappers around essential oil bag. However, the yields of the 6:1 (11.67 ± 0.00%v/w) and 7:1

(10.78 ± 0.09%v/w) mL/g showed a descending trend due to the excess amount of water ratio because in essential oil consist of esters which they tend to react with water to from acids and alcohols [49]. Therefore, the excess amount of water resulting in a decreased yield of essential oil. According to the results, we selected the ratio of 5:1 mL/g to study the effect of extraction temperature and extraction time. The result was similar to the others research such as, T P Dao et al, 2020 [32] also found that in the range of 3:1, 4:1, 5:1, 6:1 and 7:1 mL/g solid to water ratio, the optimum value is 5:1 mL/g optimized by a central composite design (CCD).

4.1.2 Effect of extraction temperature and extraction time

The process is operated with temperature at 130, 140, and 150 °C with extraction time in the range of 20-300 min at optimized water to solid ratio, 5:1 mL/g, which is control variable for this process.

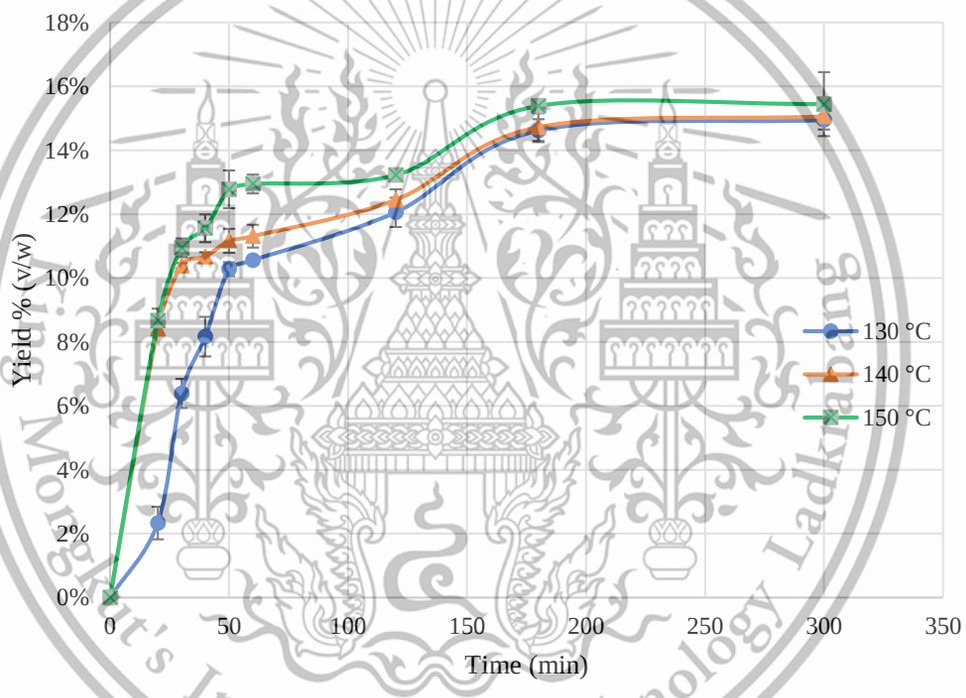


Figure 4.2 Effect of extraction temperature along with extraction time to the yields of essential oils at water to solid ratio of 5:1 mL/g.

Figure 4.2 showed that the yield increases with increasing temperature. During the heating process, water is penetrated into the oil bag and results in a rise in the vapor mixture (steam and extractable oil). In the range of temperature studied, there is only a slight difference in the obtained yield. However, the trend still showed that higher rate is observed with higher temperature identify by steeper slope. At lower temperature, steam travel through the *Z. limonella* powder slowly, where the pressure at this point is not adequate to completely extract essential oil from the *Z. limonella* powder. On the other hand, when temperature increases, the essential oil will break out resulting in higher yield. In the experiment, after 200 min of extraction the yield of essential oil reached a constant yield because the process reached equilibrium. This points out that

the rate of removal essential oil is dependent on the extraction temperature along with extraction time.

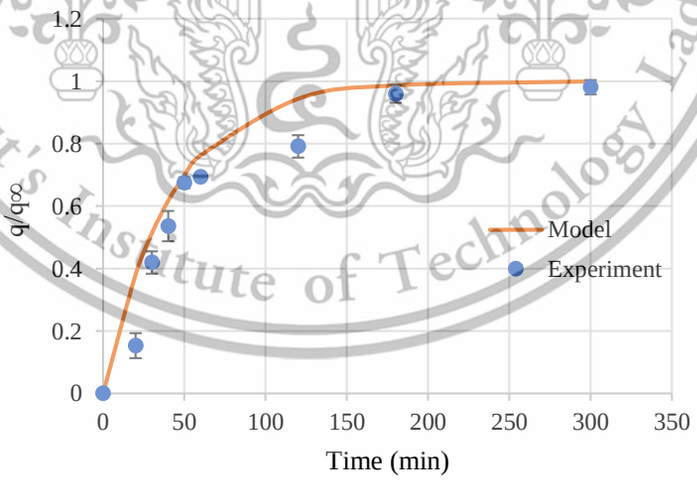
4.2 Kinetics models for hydro-distillation

Three kinetics models were applied to evaluate the appropriate model to fit with experiment data in order to predict the yield of obtained essential oil from *Z. limonella* essential oil extraction using hydro-distillation process. The three models consisted of pseudo-first order kinetics model, simultaneous washing and diffusion model, and instantaneous washing followed by diffusion model. The models investigated the influence of temperature along with time, by using 130 °C, 140 °C, and 150 °C with 20, 30, 40, 50, 60, 120, 180, and 300 min.

The mathematical model was validated according to the R^2 and the root mean square error are used to validate the mathematical model. Furthermore, the error coefficient was also used as the deviation measure. The error coefficient (C_e) was computed as $C_e = (\sum_{i=1}^{n} \frac{|Y_i - z_i|}{n})/\bar{Y}$, where Y_i is the i^{th} observed value obtained in the experiments, z_i is the i^{th} value predicted by the mathematical model, $\bar{Y}$ is the average of the observed values, and n is the number of experiments performed. The C_e close to zero indicates a good fit for the model.

4.2.1 Pseudo-first order kinetics model

This is the simplest model. In pseudo-first order model, the washing of the essential oil stage is not included in the model which a fraction of the essential oil that located at the external surfaces of the plant particles is not available ($f = 0$) in the eqn (2).



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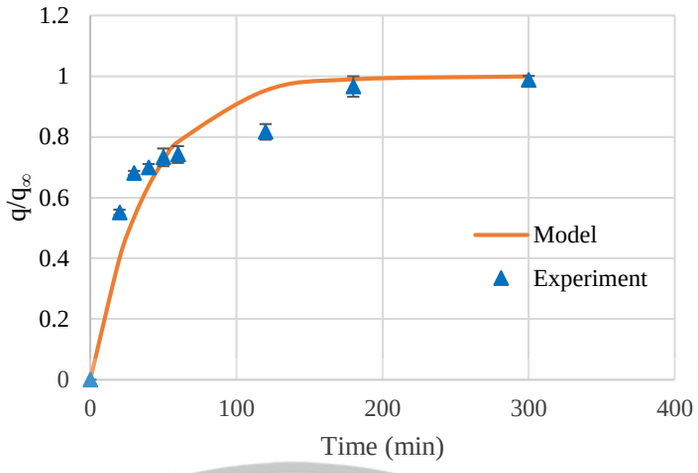

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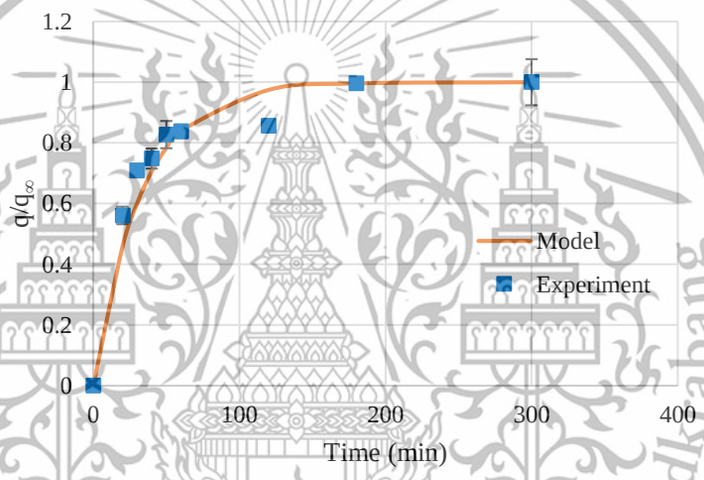


c)

Figure 4.3 The effect of temperature and time on q/q_∞ during hydro-distillation. All experiments were performed with 5:1 mL/g water to solid ratio and using pseudo-first order kinetics model to predict values; a) temperature at 130 °C, b) temperature at 140 °C, and c) temperature at 150 °C

From Figure 4.3 the graphs showed that due to the increasing of the time and temperature, the value of q/q_∞ are also increased which related to the amount of essential oil present in the process. Although the model was assuming as no washing step in the process, the experiment data are fairly close to the predicted line.

Table 4.1 Parameters of pseudo-first order model for *Z. limonella* essential oil extraction by hydro-distillation

Temperature (°C)	k_2	R^2	RMSE	C_e
130	0.0239	0.9753	0.1174	2.2375
140	0.0255	0.9830	0.0996	0.8764
150	0.0306	0.9911	0.0757	0.6752

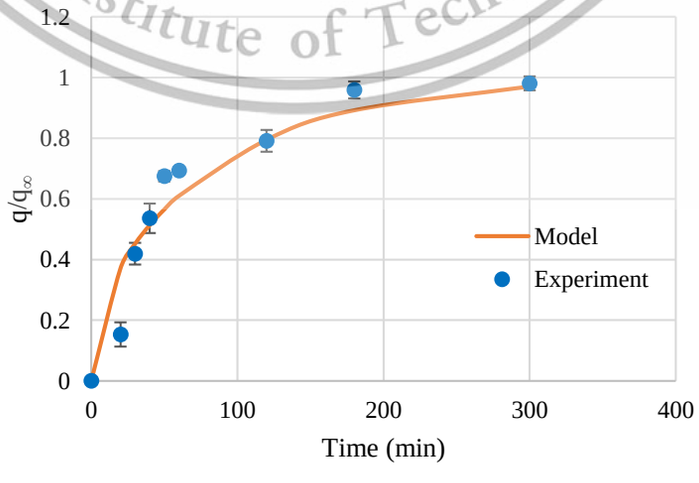
Table 4.1 represent the variable parameters from Equation (2)

$$q_L = q_{Le}(1 - \exp(-kt)) \quad (2)$$

According to the Table 4.1, showed parameters in pseudo-first order model including coefficient of determination (R^2) are 0.9753, 0.9830, and 0.9911 for 130 °C, 140 °C, and 150 °C, respectively. For the root mean square error (RMSE) are 0.1174, 0.0994, and 0.0757 for 130 °C, 140 °C, and 150 °C, respectively, and the error coefficient (C_e) are 2.2375, 0.8764, and 0.6752 for 130 °C, 140 °C, and 150 °C, respectively. The experiment data fitted quite well especially at temperature of 150 °C. For the rate constants for diffusion processed (k_2) of 130 and 140 °C are close to each other and k_2 of 150 °C is the highest value.

4.2.2 Simultaneous washing and diffusion model

The model of simultaneous washing and diffusion assumes that the isolation of essential oil occurs via two simultaneous mechanisms: washing of essential oils from the external surface of plant particles and diffusion of essential oils from inside the plant particles to the external surface. The kinetics of these two processes are assumed to follow a first-order with respect to essential oils in plant particles.



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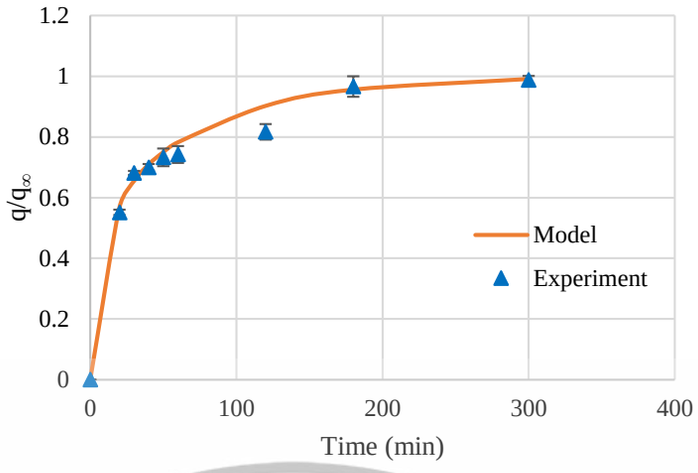

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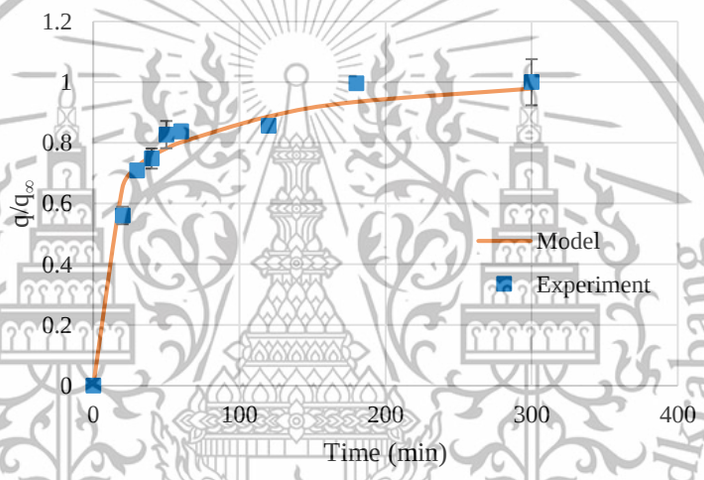


c)

Figure 4.4 The effect of temperature and time on q/q_∞ during hydro-distillation. All experiments were performed with 5:1 mL/g water to solid ratio and using simultaneous washing and diffusion model to predict values; a) temperature at 130 °C, b) temperature at 140 °C, and c) temperature at 150 °C

Figure 4.4 shows the approximation between the predicted line values from simultaneous washing and diffusion model and the experiment data, which fitted well in all temperature. The initial stage showed rapid increasing of essential oil and then slowly became constant due to the reaching of equilibrium point. The graphs showed that when temperatures rise, the content of volatile oil tends to rise along with time, this is because the elevated temperature improved penetrability and solubility of solvent which could result in higher yields.

Table 4.2 Parameters of simultaneous washing and diffusion model for *Z. limonella* essential oil extraction by hydro-distillation.

Temperature (°C)	k_1	k_2	f	R^2	RMSE	C_e
130	0.1050	0.0107	0.260	0.9762	0.1017	1.9672
140	0.1044	0.0133	0.520	0.9977	0.0385	0.2836
150	0.1188	0.0093	0.655	0.9964	0.0495	0.4764

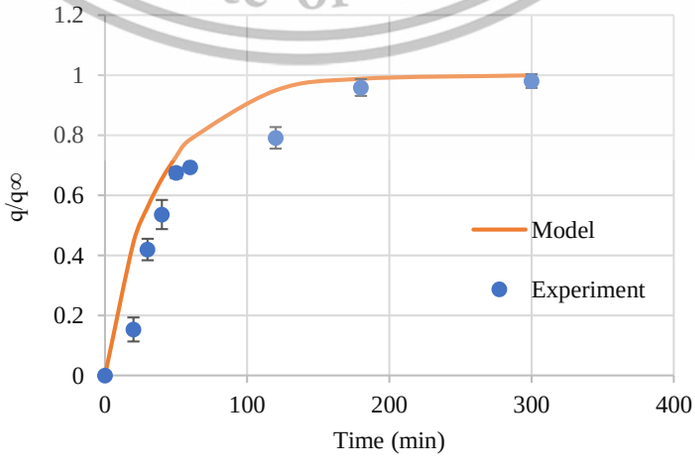
Table 4.2 represent the variable parameters from Equation (8)

$$\frac{q_p}{q_\infty} = fe^{-k_1 t} + (1-f)e^{-k_2 t} \quad (8)$$

Table 4.2 showed parameters in simultaneous washing and diffusion model consists of coefficient of determination (R^2) are 0.9762, 0.9977, and 0.9964 for 130 °C, 140 °C, and 150 °C, respectively, which showed the preciseness between experiment and predicted values. In addition, the root mean square error (RMSE) are 0.1017, 0.0385, and 0.0495 for 130 °C, 140 °C, and 150 °C, respectively, and showed values of the error coefficient (C_e) values which are 1.9672, 0.2836, and 0.4764 for 130 °C, 140 °C, and 150 °C, respectively. Hence, the simultaneous washing and diffusion model is suitable for predicting the amount of essential oil.

4.2.3 Instantaneous washing followed by diffusion model

According to the instantaneous washing followed by diffusion model, essential oils are separated in two consecutive steps. In the first step, the essential oil is washed from the external surface of the plant particles, and then it diffuses from the inside of the plant particles to the external surface. The kinetics of both these processes are assumed to follow a first-order, which is similar to the model of simultaneous washing and diffusion.



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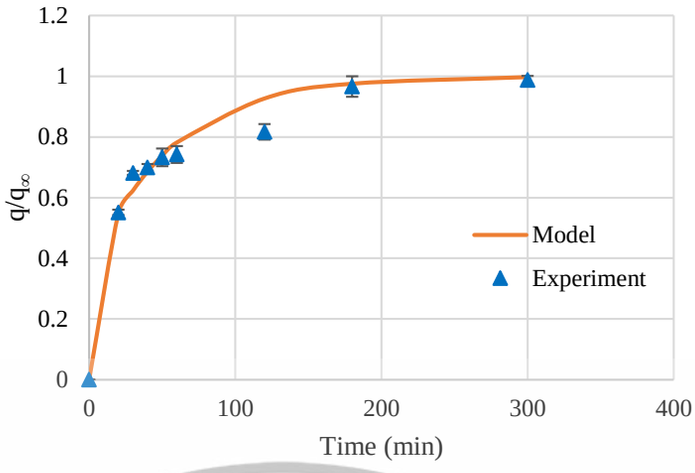

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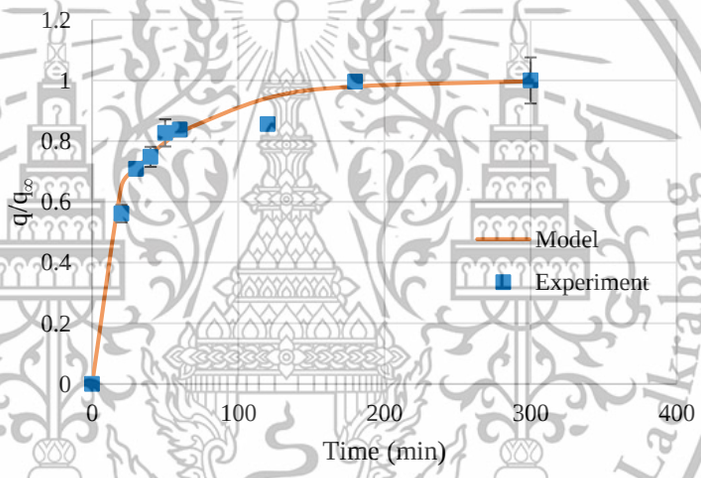

c)

Figure 4.5 The effect of temperature and time on q/q_∞ during hydro-distillation. All experiments were performed with 5:1 mL/g water to solid ratio and using instantaneous washing followed by diffusion model to predict values; a) temperature at 130 °C, b) temperature at 140 °C, and c) temperature at 150 °C.

Figure 4.5 shows that using instantaneous washing followed by diffusion model compared with the experimental results can be used only in the latter stage of water distillation, the diffusion step, because the error is relatively small compared to the first washing step that has the error majority, additionally the model performs well at higher temperatures due to the facilitation of rapid water passage through the walls of *Z. limonella*. This suggests that the washing process occurs quickly under these conditions. At an extraction time of 20 minutes, the experimental values were quite different from the values obtained from the model.

Table 4.3 Parameters of instantaneous washing followed by diffusion model for *Z. limonella* essential oil extraction by hydro-distillation.

Temperature (°C)	k_2	f	R^2	RMSE	C_e
130	0.0239	0.100	0.9630	0.1491	2.9178
140	0.0182	0.350	0.9960	0.0499	0.3762
150	0.0179	0.500	0.9966	0.0490	0.4516

Table 4.3 represent the variable parameters from Equation (11)

$$\frac{q}{q_\infty} = 1 - (1 - f)e^{-k_2 t} \quad (11)$$

Table 4.3 presents the variable parameters in the immediate wash followed by the diffusion model, with the coefficient of determination (R^2) are 0.9630, 0.9960, and 0.9966 for 130 °C, 140 °C, and 150 °C, respectively, indicating a relatively low value. On the other hand, the root mean square error (RMSE) is relatively high, which are 0.1491, 0.0499, and 0.0490 for 130 °C, 140 °C, and 150 °C, respectively. However, the coefficients of error (C_e) at temperatures 140°C and 150°C were less than 0.5, specifically 0.3762 and 0.4516, respectively, indicating that the model was more reliable at higher temperatures, as the washing mechanism was more effective. In contrast, the coefficient of error (C_e) at 130°C had a large value of 2.9178, and the predicted line is closely aligned with the experimental values. The rate constant for diffusion (k_2) is considered reliable, as the rate constant for diffusion in various plant materials typically falls within the range of 0.01 to 0.02 min^{-1} [15]. Furthermore, increasing the temperature from 130 to 150 °C results in an increase in the f value from 0.100 to 0.500, indicating a greater proportion of essential oils available for washing due to increased temperature, which in turn causes more cell wall destruction [50].

Comparing the three models, the simultaneous washing and diffusion model is the most accurate fit due to the highest coefficient of determination (R^2) and has the lowest of RMSE and C_e among three models. In addition, it was found that the model was more reliable at higher temperatures. Tan Phat Dao et al, 2021 [50] also studied the kinetics modeling of essential oil using hydro-distillation from peels of pomelo fruit, the result showed that the simultaneous washing and diffusion model is the best appropriate model to describe the mechanism of hydro-distillation.

4.3 Thermodynamics parameters

The Arrhenius model can be represented in linear form as $\ln k = \ln(A) - \frac{Ea}{R}\frac{1}{T}$, where k is the extraction rate constant, T (K) is the absolute temperature of the extraction process, R (8.314 kJ/mol.K) is the gas constant, A is the Arrhenius constant, and Ea (kJ/mol) is the activation energy of extraction. This model can be used to

investigate the dependence of the rate constants of the extraction process on temperature. The rate constants of the Pseudo-first order kinetics model was used to investigate the dependent relationship between the rate constants on temperature. The k value obtained from the Pseudo-first order kinetics model can be compared to the k value obtained by the Arrhenius model, which is an inverse function of temperature. Based on this comparison, the Arrhenius model was considered sufficient to demonstrate the dependent relationship between the rate constants on temperature [38,39]

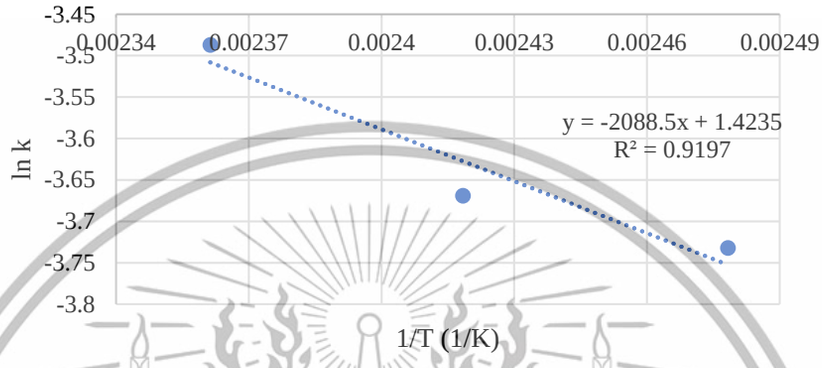

Figure 4.6 Plot of lnk versus the reciprocal of the temperature (1/T)

Based on figure 4.6 it can be observed that there is a linear relationship between lnk and 1/T with an R^2 value of 0.9197. The Arrhenius constant A is determined to be 4.1516 and the activation energy for extraction. The calculated Ea of 17.3638 kJ/mol is considered to be within the range of 14.65-22.74 kJ/mol which is reported by S.B. Santos et al, 2015 [36]. These values indicate that the extraction process is endothermic in nature.

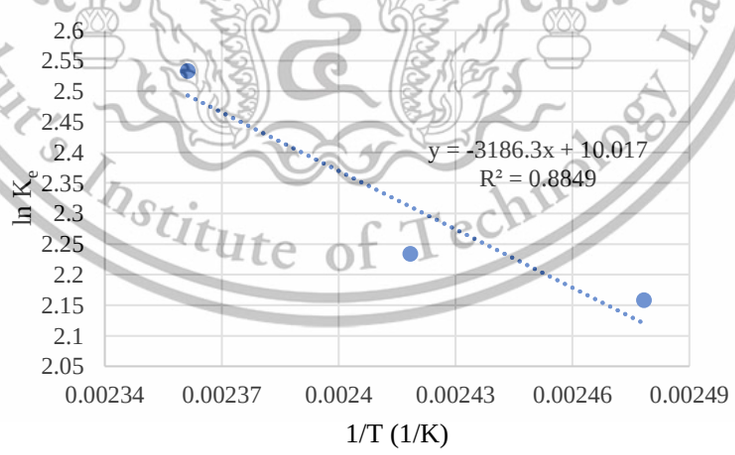

Figure 4.7 Plot of ln K_e versus the reciprocal of the temperature (1/T)

The differential enthalpy (ΔH°) and differential entropy (ΔS°) were obtained from the ratio of the natural logarithm of the equilibrium constant of the extraction process (k) to the inverse temperature (1/T) using the Van't Hoff equation (12). Based on figure 4.7 it can be observed that the relationship between the values of ln K_e and 1/T is linear with a coefficient of determination (R^2) of 0.8849.

$$\ln K = \frac{-\Delta H^\circ}{R}\frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (12)$$

Table 4.4 Thermodynamics parameters for extraction of *Z. limonella* oil

Temperature (°C)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)	K_e	ΔG° (kJ/mol)
130	26.4909	83.2813	8.6544	-7.1131
140			9.3326	-7.9459
150			12.5896	-8.7788

Based on the data in Table 4.4, the values of ΔH° and ΔS° for the extraction of *Z. limonella* oil were found to be positive within the range of extraction temperatures. This suggests that the extraction process was endothermic due to positive ΔH° and irreversible in nature due to positive ΔS°. Furthermore, the negative value of the Gibbs free energy (ΔG°) indicates that the extraction process was viable and spontaneous nature under the given conditions.

4.4 Prediction of the concentration of important active components using the UNIFAC model and modified Raoult's law

The concentration of active components was predicted using the modified Raoult's law, Equation (15), by determining the vapor fraction (y_i) while considering the activity coefficients derived from the UNIFAC model, Equation (17-28), for comparison with the experimental values.

Table 4.5 Experimental and predicted constituents mole fraction and UNIFAC-predicted activity coefficients for *Z.limonella* essential oil at water to solid ratio of 5:1 mL/g with extraction time 2 h for temperature 130°C, 140°C and 150°C

Temperature	**130 °C**		
Constituents	Experiment	Thermodynamics model	Activity Coefficient
	Mole fraction %	Mole fraction %	
Limonene	40.54	40.83	1.010
Sabinene	29.13	29.70	1.028
Others	30.33	29.47	1.018
Temperature	**140 °C**		
Limonene	41.57	40.60	1.017
Sabinene	32.17	32.22	1.019
Others	26.26	27.18	1.027
Temperature	**150 °C**		
Limonene	40.47	40.00	1.023
Sabinene	33.33	33.21	1.013
Others	26.20	26.78	1.035

From Table 4.5, it can be observed that the mole fractions obtained from the experiment and the modified Raoult's law were very close. Therefore, it can be concluded that the modified Raoult's law equation can be used to predict the concentration of essential substances in the extraction by hydro-distillation.

4.5 Chromatographic analyses of essential oil

The essential oil of *Z. limonella* fruits were extracted by hydro-distillation process using 5:1 mL/g with 2 h and temperature of 130°C, 140°C and 150°C, respectively. Chemical constituents were characterized through GC-MS, the identified constituents, and the percentage yield of *Z. limonella* essential oil extracted at 130°C are listed in Table 4.6. The main components are limonene 40.54%, sabinene 29.13%, and the rest are in the trace amount. Table 4.7 the main components extracted at 140°C are limonene 41.58%, sabinene 32.17%, and the rest are in the trace amount. Table 4.8 the main components extracted at 150°C are limonene 40.47%, sabinene 33.33%, and the rest are in the trace amount.

Table 4.6 Chemical composition of *Z. limonella* essential oil at 130°C

No.	R.T. min	Compounds	Percent
1	6.20	Thujene	0.42
2	6.33	α-Pinene	3.06
3	7.13	Sabinene	29.13
4	7.17	β-Pinene	0.07
5	7.41	β-Myrcene	2.13
6	7.67	1-Phellandrene	5.64
7	7.77	3-Carene	0.20
8	7.89	α-Terpinene	0.52
9	8.04	Benzene	2.47
10	8.15	Limonene	40.54
11	8.25	cis-Ocimene	0.95
12	8.44	1,3,6-Octatriene	4.06
13	8.64	γ-Terpinene	0.88
14	8.78	cis-Sabinenehydrate	0.28
15	9.14	α-Terpinolene	0.31
16	9.27	2-Methyladamantane	0.03
17	9.31	1,6-Octadien-3-ol	0.61
18	9.38	Nonanal	0.04
19	9.70	cis-Sabinenehydrate	0.28

No.	R.T. min	Compounds	Percent
20	9.91	p-mentha-E-2,8(9)-dien-1-ol	0.12
21	9.99	4-Carene	0.24
22	10.29	Bicyclo[3.1.0]hexan-2-one, 5-(1-methylethyl)-	0.08
23	10.45	Nonanol	0.12
24	10.60	3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-	2.04
25	10.70	Bicyclo(3.1.1)hept-2-ene-2-carboxaldehyde, 6,6-dimethyl-	0.07
26	10.74	2-Cyclohexen-1-ol, 1-methyl-4-(1-methylethyl)-	0.23
27	10.80	α-Terpineol	0.77
28	10.88	2-Cyclohexen-1-ol, 3-methyl-6-(1-methylethyl)-	0.08
29	10.98	Decanal	0.53
30	11.05	Acetic acid	0.75
31	11.22	trans-Carveol	0.24
32	11.39	2-Cyclohexen-1-ol, 2-methyl-5-(1-methylethenyl)-	0.10
33	11.55	Benzaldehyde, 4-(1-methylethyl)-	0.04
34	11.60	2-Cyclohexen-1-one, 2-methyl-5-(1-methylethyl)-	0.25
35	11.70	Farnesol	0.09
36	11.94	1-Decanol	0.10
37	12.21	Endobornyl Acetate	0.04
38	12.26	2-Undecanone	0.29
39	12.64	2-Acetylcyclopentanone	0.06
40	13.23	Geranyl acetate	0.05
41	13.48	2,6-Octadien-1-ol, 3,7-dimethyl-	0.97
42	13.82	Cyclodecane	0.29
43	13.89	Benzene, 1,3-diethyl-	0.03
44	14.10	trans-Caryophyllene	0.40
45	14.54	α-Humulene	0.04
46	14.88	Germacrene-D	0.15
47	14.92	2-Tridecanone	0.06

No.	R.T. min	Compounds	Percent
48	16.15	(-)-Caryophyllene oxide	0.09
49	16.26	Cyclododecane	0.06

Table 4.7 Chemical composition of *Z. limonella* essential oil at 140°C

No.	R.T. min	Compounds	Percent
1	6.20	Thujene	0.42
2	6.34	α-Pinene	3.03
3	7.10	Sabinene	32.17
4	7.42	β-Myrcene	1.90
5	7.67	1-Phellandrene	4.90
6	7.78	3-Carene	0.21
7	7.89	α-Terpinene	0.44
8	8.03	Benzene	2.68
9	8.11	Limonene	41.58
10	8.26	cis-Ocimene	0.80
11	8.44	1,3,6-Octatriene	3.40
12	8.64	γ-Terpinene	0.82
13	8.78	cis-Sabinenehydrate	0.19
14	9.15	α-Terpinolene	0.25
15	9.27	β-Pinene	0.01
16	9.32	1,3,6-Octatriene	0.52
17	9.70	5-methylenecyclononanone	0.21
18	9.81	β-Pinene	0.02
19	10.00	4,5-Nonadiene	0.20
20	10.60	3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-	1.98
21	10.75	2-Cyclohexen-1-one, 2-methyl-5-(1-methylethyl)-	0.20
22	10.80	β-Fenchyl Alcohol	0.70
23	10.88	cis-Sabinenehydrate	0.08
24	10.98	Decanal	0.35
25	11.05	Acetic acid	0.65

No.	R.T. min	Compounds	Percent
26	11.22	trans-Carveol	0.15
27	11.40	2-Cyclohexen-1-ol, 2-methyl-5-(1-methylethenyl)-	0.04
28	11.56	Ethanone	0.02
29	11.60	2-Cyclohexen-1-one, 2-methyl-5-(1-methylethyl)-	0.20
30	11.70	4-Methyl-2,3-hexadien-1-ol	0.05
31	11.96	Acetonitrile, 2,2'-iminobis-	0.02
32	12.26	2-Undecanone	0.16
33	13.48	Acetamide	0.60
34	13.69	Propanoic acid	0.01
35	13.82	Cyclodecane	0.14
36	14.10	trans-Caryophyllene	0.30
37	14.88	Germacrene-D	0.10
38	14.93	2-Octanone	0.03
39	16.15	Cyclohexane	0.03
40	16.26	Acetic acid	0.02
41	20.06	3-Pentanol, 2-methyl- (CAS)	0.02
42	24.41	9-Octadecenamide	0.24

Table 4.8 Chemical composition of *Z. limonella* essential oil at 150°C

No.	R.T. min	Compounds	Percent
1	6.20	Thujene	0.40
2	6.34	α-Pinene	2.69
3	7.10	Sabinene	33.33
4	7.42	β-Myrcene	1.74
5	7.67	1-Phellandrene	4.10
6	7.78	3-Carene	0.18
7	7.89	α-Terpinene	0.34
8	8.03	Benzene	2.51
9	8.11	Limonene	40.47
10	8.26	cis-Ocimene	0.71

No.	R.T. min	Compounds	Percent
11	8.44	1,3,6-Octatriene	3.24
12	8.64	γ-Terpinene	0.67
13	8.78	cis-Sabinenehydrate	0.37
14	9.15	α-Terpinolene	0.21
15	9.32	β-Pinene	0.61
16	9.70	1,3,6-Octatriene	0.27
17	9.91	5-methylenecyclononanone	0.14
18	10.00	β-Pinene	0.23
19	10.29	4,5-Nonadiene	0.06
20	10.60	3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-	2.04
21	10.70	Benzaldehyde, 4-(1-methylethyl)-	0.08
22	10.75	2-Cyclohexen-1-one, 2-methyl-5-(1-methylethyl)-	0.24
23	10.80	β-Fenchyl Alcohol	0.90
24	10.89	cis-Sabinenehydrate	0.11
25	10.98	Decanal	0.40
26	11.05	Acetic acid	0.68
27	11.22	trans-Carveol	0.24
28	11.40	2-Cyclohexen-1-ol, 2-methyl-5-(1-methylethenyl)-	0.07
29	11.56	Ethanone	0.04
30	11.60	2-Cyclohexen-1-one, 2-methyl-5-(1-methylethyl)-	0.30
31	11.70	4-Methyl-2,3-hexadien-1-ol	0.08
32	12.22	Acetamide	0.03
33	12.26	2-Undecanone	0.24
34	12.64	2-Cyclopentene-1-thione	0.03
35	13.22	Acetamide	0.03
36	13.48	Propanoic acid	0.75
37	13.82	Cyclodecane	0.20
38	14.10	trans-Caryophyllene	0.40
39	14.55	β-Pinene	0.03

No.	R.T. min	Compounds	Percent
40	14.88	Germacrene-D	0.11
41	14.93	2-Octanone	0.05
42	16.15	Cyclohexane	0.08
43	16.26	Acetic acid	0.04
44	22.17	3-Pentanol, 2-methyl- (CAS)	0.04
45	24.41	9-Octadecenamide	0.52

CHAPTER V

CONCLUSIONS

In this study, the extract of *Z. limonella* fruits using hydro-distillation process, was studied to evaluate the optimal conditions as factors affecting the process yield, including water to solid extraction ratio, extraction temperature, and extraction time. Furthermore, three process kinetics models were studied in order to identify a suitable model for *Z. limonella* oil extraction. In addition, thermodynamics parameters and the predictive thermodynamics method (UNIFAC) to estimate the active constituents for each temperature were studied. Finally, amount of active components in essential oil quality was assessed based on GC-MS analysis.

The *Z. limonella* oil is extracted at optimum condition at water to solid ratio of 5:1 mL/g using 150°C and 180 min of extraction time which showed yield of 15.39 ± 0.25%(v/w). The simultaneous washing and diffusion model was suitable kinetics model. This model gave the most accurate trends with the highest correlation coefficient (R^2) with the lowest RMSE and C_e. In addition, the activation energy (Ea) for extraction is 17.3638 kJ/mol and the differential enthalpy and entropy were positive which indicated that system is endothermic and irreversible. The predictive mole fraction of active components at different temperature using UNIFAC method were good prediction compared to experimental data at all temperature (130°C, 140°C, and 150°C) studied.

Suggestion

- The other physical properties of *Z. limonella* essential oil such as dielectric constant, polarity and solubility should be examined to identify the optimum extraction properties.
- Further studies should be undertaken at various temperatures to obtain enough information for the thermodynamics and kinetic models to be used in further studies.
- Concentration prediction studies of other compounds in *Z. limonella* essential oil, such as terpinen-4-ol, should be performed. This is useful for other industries as terpinen-4-ol has been proven to be effective against bacteria that cause acne and reduce inflammation.
- The optimal conditions for extracting essential oil from *Z. limonella* can be further utilized as a safe and beneficial mosquitoes repellent.

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APPENDIX

APPENDIX A

A.1 Raw data effect of water to solid ratio for *Z.limonella* essential extraction effect

Table A.1a Raw data at 150°C with the water to solid ratio of 2:1, 3:1, 4:1, 5:1, 6:1 and 7:1 mL/g. The extraction time 60 minutes, and the yields were expressed as percentage by volume per weight (v/w).

Water to solid ratio (mL/g)	Yield % (v/w)			Average	SD
	Trial 1	Trial 2	Trial 3		
2:1	10.00	9.67	10.00	9.89	0.0019
3:1	10.67	11.67	11.67	11.34	0.0058
4:1	11.67	11.67	11.67	11.67	0.0000
5:1	12.83	12.67	13.33	12.94	0.0034
6:1	11.67	11.67	11.67	11.67	0.0000
7:1	10.83	10.67	10.83	10.78	0.0009

Table A.1b Raw data at 150°C with the water to solid ratio of 2:1, 3:1, 4:1, 5:1, 6:1 and 7:1 mL/g. The extraction time 60 minutes, and the yields were expressed as percentage by weight per weight (w/w).

Water to solid ratio (mL/g)	Yield % (w/w)			Average	SD
	Trial 1	Trial 2	Trial 3		
2:1	8.53	8.25	8.53	8.44	0.1642
3:1	9.10	9.95	9.95	9.67	0.4925
4:1	9.95	9.95	9.67	9.86	0.1642
5:1	10.95	10.80	11.37	11.04	0.2959
6:1	9.95	9.95	9.95	9.95	0.0000
7:1	9.24	9.10	9.24	9.19	0.0821

A.2 Raw data effect of extraction temperature for *Z.limonella* essential extraction effect

Table A.2a Raw data 5:1 mL/g water to solid ratio at the extraction time 60 minutes with temperature of 130°C, 140°C and 150°C, and the yields were expressed as percentage by volume per weight (v/w).

Temperature (°C)	Yield % (v/w)			Average	SD
	Trial 1	Trial 2	Trial 3		
130	10.50	10.50	10.67	10.56	0.0010
140	11.60	10.83	11.50	11.31	0.0042
150	12.83	12.67	13.33	12.94	0.0034

Table A.2b Raw data 5:1 mL/g water to solid ratio at the extraction time 60 minutes with temperature of 130°C, 140°C and 150°C, and the yields were expressed as percentage by weight per weight (w/w).

Temperature (°C)	Yield % (w/w)			Average	SD
	Trial 1	Trial 2	Trial 3		
130	8.96	8.96	9.10	9.00	0.0008
140	9.89	9.24	9.81	9.65	0.0036
150	10.94	10.81	11.37	11.04	0.0029

A.3 Raw data of optimum condition to create kinetics model for extraction

The kinetics models for *Z.limonella* using hydro-distillation extraction were selected as a simultaneous washing and diffusion mode. This studied the influences of temperature at 130, 140, 150 °C with the extraction time of 20, 30, 40, 50, 60, 120, 180 and 300 minutes at 5:1 mL/g water to solid ratio were determined in this experiment.

Table A.3.1a Raw data at 130°C with the extraction time 20, 30, 40, 50, 60, 120, 180 and 300 minutes with 5:1 mL/g water to solid ratio and the yields were expressed as percentage by volume per weight (v/w).

Times (min)	Yield % (v/w)			Average	SD
	Trial 1	Trial 2	Trial 3		
20	2.83	1.67	2.50	2.33	0.0060
30	7.00	6.17	6.00	6.39	0.0054
40	7.83	7.67	9.00	8.17	0.0073
50	10.00	10.33	10.50	10.28	0.0025
60	10.50	10.50	10.67	10.56	0.0010
120	11.83	12.67	11.67	12.06	0.0054
180	14.67	14.17	15.00	14.61	0.0042
300	14.83	15.33	14.67	14.94	0.0034

Table A.3.1b Raw data at 130°C with the extraction time 20, 30, 40, 50, 60, 120, 180 and 300 minutes with 5:1 mL/g water to solid ratio and the yields were expressed as percentage by weight per weight (w/w).

Times (min)	Yield % (w/w)			Average	SD
	Trial 1	Trial 2	Trial 3		
20	2.41	1.42	2.13	1.99	0.0051
30	5.97	5.26	5.12	5.45	0.0046
40	6.68	6.54	7.68	6.97	0.0062
50	8.53	8.81	8.96	8.77	0.0022
60	8.96	8.96	9.10	9.00	0.0008
120	10.09	10.81	9.95	10.28	0.0046
180	12.51	12.09	12.80	12.47	0.0036
300	12.65	13.08	12.51	12.75	0.0029

Table A.3.2a Raw data at 140°C with the extraction time 20, 30, 40, 50, 60, 120, 180 and 300 minutes with 5:1 mL/g water to solid ratio and the yields were expressed as percentage by volume per weight (v/w).

Times (min)	Yield % (v/w)			Average	SD
	Trial 1	Trial 2	Trial 3		
20	8.33	8.33	8.56	8.41	0.0013
30	10.33	10.50	10.33	10.39	0.0010
40	10.83	10.67	10.50	10.67	0.0017
50	11.33	10.67	11.50	11.17	0.0044
60	11.60	10.83	11.50	11.31	0.0042
120	12.67	12.67	12.00	12.45	0.0039
180	14.17	14.83	15.17	14.72	0.0051
300	15.17	14.83	15.17	15.06	0.0020

Table A.3.2b Raw data at 140°C with the extraction time 20, 30, 40, 50, 60, 120, 180 and 300 minutes with 5:1 mL/g water to solid ratio and the yields were expressed as percentage by weight per weight (w/w).

Times (min)	Yield % (w/w)			Average	SD
	Trial 1	Trial 2	Trial 3		
20	7.11	7.11	7.30	7.17	0.001133
30	8.81	8.96	8.81	8.86	0.000837
40	9.24	9.10	8.96	9.10	0.001408
50	9.66	9.10	9.81	9.53	0.003740
60	9.89	9.24	9.81	9.65	0.003571
120	10.81	10.81	10.24	10.62	0.003300
180	12.09	12.65	12.94	12.56	0.004337
300	12.94	12.65	12.94	12.84	0.001674

Table A.3.3a Raw data at 150°C with the extraction time 20, 30, 40, 50, 60, 120, 180 and 300 minutes with 5:1 mL/g water to solid ratio and the yields were expressed as percentage by volume per weight (v/w).

Times (min)	Yield % (v/w)			Average	SD
	Trial 1	Trial 2	Trial 3		
20	8.16	8.83	9.00	8.66	0.0044
30	10.67	10.83	11.33	10.94	0.0034
40	12.00	11.67	11.00	11.56	0.0051
50	13.00	13.33	12.00	12.78	0.0069
60	12.83	12.67	13.33	12.94	0.0034
120	13.33	13.33	13.00	13.22	0.0019
180	15.66	15.17	15.33	15.39	0.0025
300	15.33	14.33	16.67	15.44	0.0117

Table A.3.3b Raw data at 150°C with the extraction time 20, 30, 40, 50, 60, 120, 180 and 300 minutes with 5:1 mL/g water to solid ratio and the yields were expressed as percentage by weight per weight (w/w).

Times (min)	Yield % (w/w)			Average	SD
	Trial 1	Trial 2	Trial 3		
20	6.96	7.53	7.68	7.39	0.003788
30	9.10	9.24	9.66	9.33	0.002937
40	10.24	9.95	9.38	9.86	0.004346
50	11.09	11.37	10.24	10.90	0.005907
60	10.94	10.81	11.37	11.04	0.002937
120	11.37	11.37	11.09	11.28	0.001625
180	13.36	12.94	13.08	13.12	0.002131
300	13.08	12.22	14.22	13.17	0.010015

APPENDIX B

B1. Sample of calculations for the pseudo-first order kinetics model at temperature 130°C

Equation (2) is rearranged to find the process rate constant (k) by plotting the slope. Therefore

$$\ln\left(\frac{q_{Le}}{q_{Le}-q_L}\right) = -kt$$

where q_L and q_{Le} represent the oil concentrations in the liquid phase at extraction time t and at equilibrium after 300 minutes of extraction, respectively.

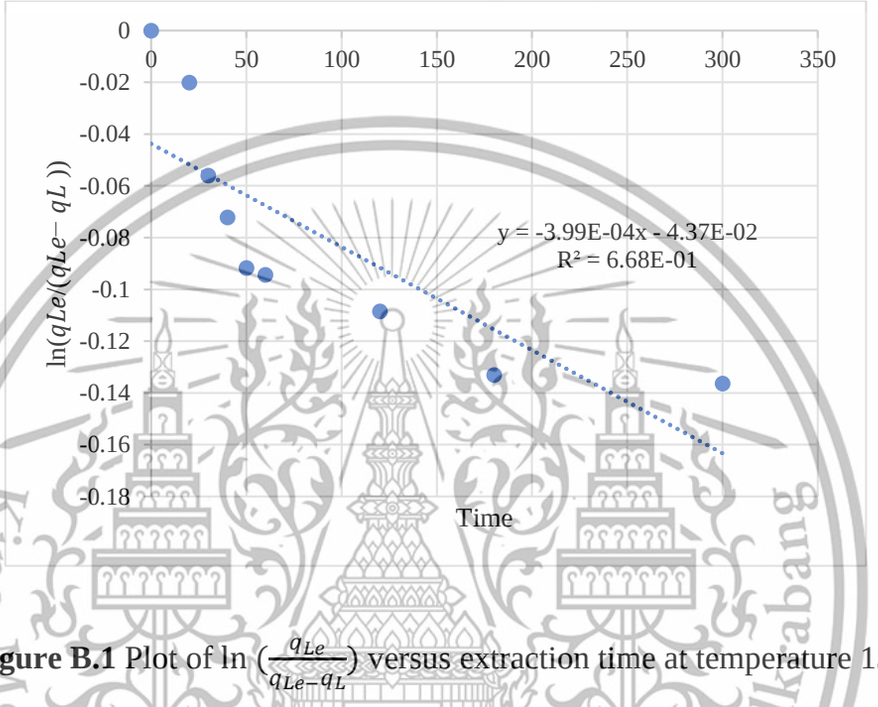

Figure B.1 Plot of ln $\left(\frac{q_{Le}}{q_{Le}-q_L}\right)$ versus extraction time at temperature 130°C

From Figure B.1 the process rate constant is found to be 0.000399 (s^{-1}) and this value is then substituted into Equation (2) to calculate the value of (q_L) at time (t).

Table B.1 Comparison of pseudo-first order kinetics model data with experimental values at 130°C, for extraction times of 20, 30, 40, 50, 60, 120, 180, and 300 minutes with a water to solid ratio of 5:1 mL/g

Time (minutes)	ln $\left(\frac{q_{Le}}{q_{Le}-q_L}\right)$	pseudo-first order kinetics equation	Experiment
0	0.0000	0.0000	0.0000
20	-0.0201	0.3805	0.1531
30	-0.0560	0.5124	0.4193
40	-0.0722	0.6162	0.5359
50	-0.0917	0.6979	0.6743
60	-0.0944	0.7622	0.6929
120	-0.1085	0.9435	0.7911
180	-0.1331	0.9866	0.9589
300	-0.1364	0.9992	0.9805

B2. Sample of calculations for the simultaneous washing and diffusion model at temperature 130°C

Equation (10) is rearranged to find the process rate constant (k) for each process by plotting the slope. Therefore,

Washing process

$$\ln\left(\frac{q_\infty}{q_\infty - q}\right) + \ln(f) = -k_1 t$$

Diffusion process

$$\ln\left(\frac{q_\infty}{q_\infty - q}\right) + \ln(1 - f) = -k_2 t$$

where q_∞ is the oil concentration in the liquid phase at equilibrium determined at 300 minutes. Since the fraction of essential oil in the equation does not affect the grade, the value is set to f=0.53.

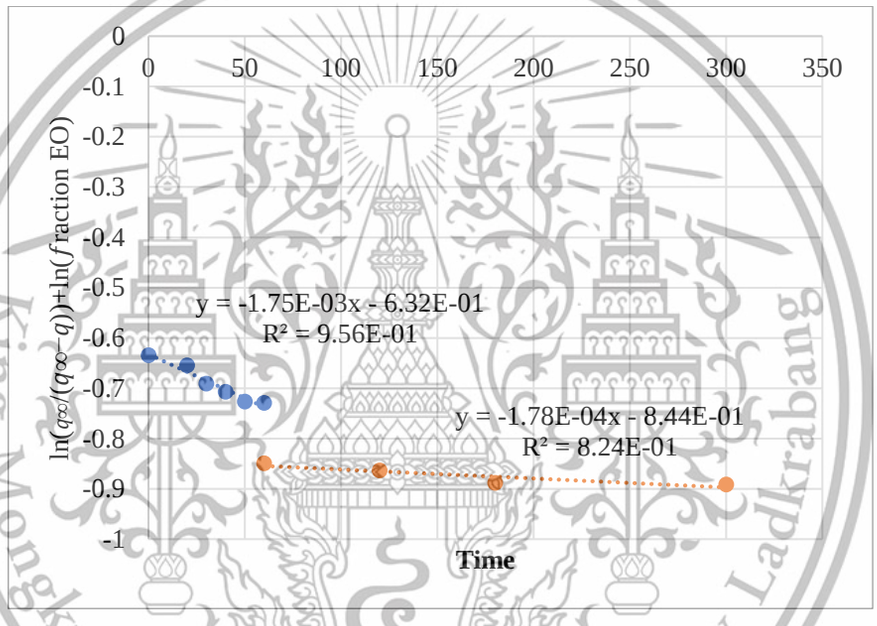

Figure B.2 Plot of $\ln\left(\frac{q_\infty}{q_\infty - q}\right) + \ln(fraction\ essential\ oil\ (EO))$ versus extraction time at temperature 130°C

From Figure B.2, the process rate constants for the washing and diffusion processes are 0.00175 (s^{-1}) and 0.000178 (s^{-1}), respectively. These values are then substituted into Equation (10) to calculate the value of (q) at time (t) by trial and error for the f value, so that the equation is as close as possible to the experimental value.

Table B.2 Comparison of simultaneous washing and diffusion model data with experimental values at 130°C, for extraction times of 20, 30, 40, 50, 60, 120, 180, and 300 minutes with a water to solid ratio of 5:1 mL/g

Time (minutes)	$\ln\left(\frac{q_\infty}{q_\infty - q}\right) + \ln\left(fraction\ EO\right)$		Simultaneous washing and diffusion equation	Experiment
	Washing	Diffusion		
0	-0.6349	-	0.0000	0.0000
20	-0.6550	-	0.3705	0.1531
30	-0.6909	-	0.4517	0.4193
40	-0.7071	-	0.5134	0.5359
50	-0.7266	-	0.5648	0.6743
60	-0.7293	-0.8494	0.6096	0.6929
120	-	-0.8635	0.7946	0.7911
180	-	-0.8882	0.8918	0.9589
300	-	-0.8914	0.9700	0.9805

B2. Sample of calculations for the instantaneous washing followed by diffusion model at temperature 130°C.

Equation (11) is rearranged to find the process rate constant (k) for diffusion process by plotting the slope. Therefore,

$$\ln\left(\frac{q_\infty}{q_\infty - q}\right) + \ln\left(1 - f\right) = -k_2 t$$

where q_∞ is the oil concentration in the liquid phase at equilibrium determined at 300 minutes. Since the fraction of essential oil in the equation does not affect the grade, the value is set to f=0.03.

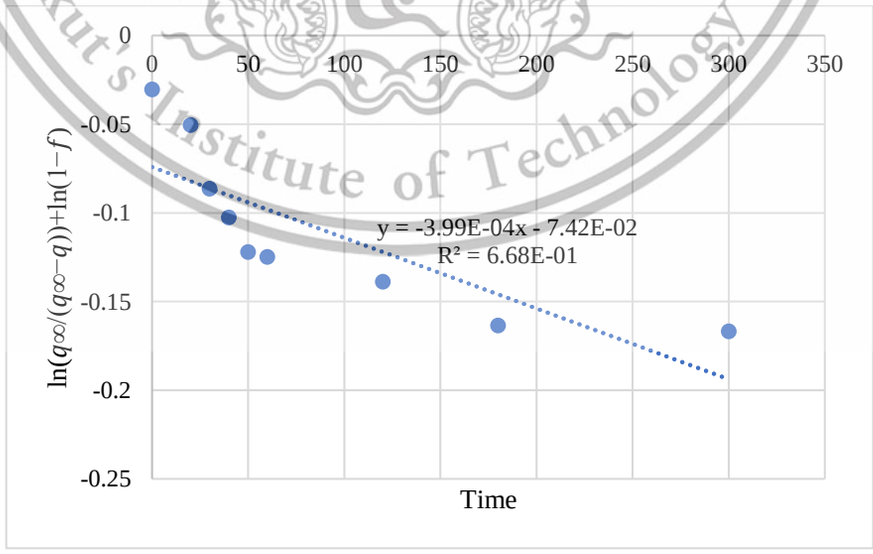

Figure B.3 Plot of $\ln\left(\frac{q_\infty}{q_\infty - q}\right) + \ln\left(1 - f\right)$ versus extraction time at temperature 130°C

From Figure B.3, the process rate constants for the diffusion processes are 0.000178 (s^{-1}). These values are then substituted into Equation (11) to calculate the value of (q) at time (t) by trial and error for the f value, so that the equation is as close as possible to the experimental value**.**

Table B.3 Comparison of instantaneous washing followed by diffusion model data with experimental values at 130°C, for extraction times of 20, 30, 40, 50, 60, 120, 180, and 300 minutes with a water to solid ratio of 5:1 mL/g

Time (minutes)	$\ln(\frac{q_\infty}{q_\infty - q}) + \ln(1-f)$	Instantaneous washing followed by diffusion equation	Experiment
0	-0.0305	0.0000	0.0000
20	-0.0506	0.4424	0.1531
30	-0.0865	0.5611	0.4193
40	-0.1027	0.6546	0.5359
50	-0.1222	0.7281	0.6743
60	-0.1249	0.7860	0.6929
120	-0.1390	0.9491	0.7911
180	-0.1636	0.9879	0.9589
300	-0.1668	0.9993	0.9805

B.4 Example of calculation of vapor fraction using modified Raoult's law and UNIFAC model at 130°C.

The vapor fractions of the active constituents of *Z. limonella* essential oil, namely limonene, sabinene, and others, were calculated. Each of these constituents has a specific chemical structure. Limonene has a structure of (CH3, CH2, C, ACCH3, ACH), sabinene has a structure of (CH3, CH2, CH, C), since the dominant of trace amount represent the formula of C10H16, it has been designated as alpha-pinene to represent the rest in trace amount, whose structure is (CH3, CH2, C, ACCH3, ACH, AC). The UNIFAC model was used to calculate the activity coefficient using equation (17-28).

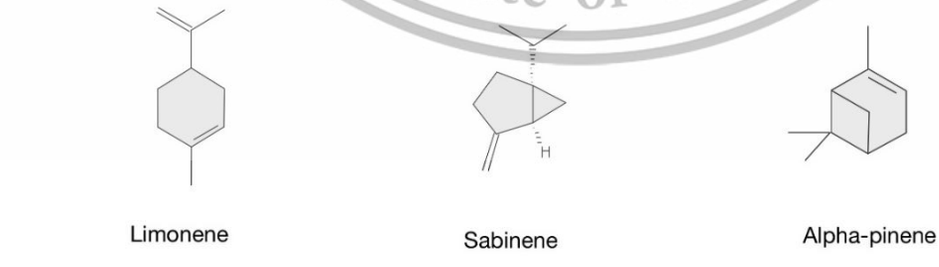

Figure B.4 Limonene, sabinene, and alpha-pinene structure.

Table B.4.1 Sub-group surface and volume parameters.

SubGroup	MainGroup		R_k	Q_k
1	1	CH_3	0.9011	0.848
2	1	CH_2	0.6744	0.54
3	1	CH	0.4469	0.228
4	1	C	0.2195	0
5	2	CH_2=CH	1.3454	1.176
6	2	CH=CH	1.1167	0.867
7	2	CH_2=C	1.1173	0.988
8	2	CH=C	0.8886	0.676
70	2	C=C	0.6605	0.485
9	3	ACH	0.5313	0.4
10	3	AC	0.3652	0.12
11	4	$ACCH_3$	1.2663	0.968
12	4	$ACCH_2$	1.0396	0.66
13	4	ACCH	0.8121	0.348
14	5	OH	1	1.2
15	6	CH_3OH	1.4311	1.432
16	7	H_2O	0.92	1.4
17	8	ACOH	0.8952	0.68
18	9	CH_3CO	1.6724	1.488
19	9	CH_2CO	1.4457	1.18
20	10	CHO	0.998	0.948
21	11	CH_3COO	1.9031	1.728
22	11	CH_2COO	1.6764	1.42
29	14	CH_2NH_2	1.3692	1.236
36	17	$ACNH_2$	1.06	0.816
42	20	COOH	1.3013	1.224
49	22	CCL_2	1.8016	1.448
51	23	CCL_3	2.6401	2.184
99	46	$CON(CH_2)_2$	2.4054	1.812

Table B.4.2 Residual group interaction parameters for main groups (a_{nm}).

SubGroup	1	2	3	4	5	6	7	8	9	10	11	14	17	20	22	23	46
1	0	86.02	61.13	76.5	986.5	697.2	1318	1333	476.4	677	232.1	391.5	920.7	663.5	53.76	24.9	380.9
2	-35.36	0	38.81	74.15	524.1	787.6	270.6	526.1	182.6	448.8	37.85	240.9	749.3	318.9	58.55	-13.99	200.2
3	-11.12	3.446	0	167	636.1	637.3	903.8	1329	25.77	347.3	5.994	161.7	648.2	537.4	-144.4	-231.9	
4	-69.7	-113.6	-146.8	0	803.2	603.2	5695	884.9	-52.1	586.6	5688	19.02	664.2	872.3	-111	-80.25	
5	156.4	457	89.6	25.82	0	-137.1	353.5	-259.7	84	-203.6	101.1	8.642	-52.39	199	65.28	-98.12	-382.7
6	16.51	-12.52	-50	-44.5	249.1	0	-181	-101.7	23.39	306.4	-10.72	359.3	489.7	-202	-102.5	-139.4	
7	300	496.1	362.3	377.6	-229.1	289.6	0	324.5	-195.4	-116	72.87	48.89	243.2	-14.09	370.4	353.7	835.6
8	275.8	217.5	25.34	244.2	-451.6	-265.2	-601.8	0	-356.1	-271.1	-449.4		119.9	408.9			
9	26.76	42.92	140.1	365.8	164.5	108.7	472.5	-133.1	0	-37.36	-213.7		6201	669.4	-130.3	-354.6	
10	505.7	56.3	23.39	106	529	-340.2	480.8	-155.6	128	0	-110.3			497.5	67.52	-483.7	
11	114.8	132.1	85.84	-170	245.4	249.6	200.8	-36.72	372.2	185.1	0		475.5	660.2	108.9	-209.7	
14	-30.48	1.163	-44.85	296.4	-242.8	-481.7	-330.4					0	-200.7				
17	1139	2000	247.5	762.8	-17.4	-118.1	-341.6	-253.1	-450.3		-294.8	-15.07	0	-396	-111		
20	315.3	1264	62.32	89.96	-151	339.8	-66.17	-11	-297.8	-165.5	-256.3		493.8	0	-44.7	39.63	-322.3
22	34.1	-23.5	121.3	140.8	527.6	669.9	708.7		82.86	190.6	-133		140.8	543.3	0	0	
23	36.7	51.06	228.5	69.9	742.1	649.1	826.8		552.1	242.8	176.5			504.2	-84.53	0	
46	27.97	9.755			394.8		-509.3							-70.25			0

Table B.4.3 Interaction parameters (a_{nm}).

Sub Group	Main Group		R_k	Q_k	1	1	1	3	3	4	4	5	6
					CH_3	CH_2	CH	ACH	AC	$ACCH_3$	$ACCH_2$	OH	CH_3OH
1	1	CH_3	0.9011	0.848	0	0	0	61.13	61.13	76.5	76.5	986.5	697.2
2	1	CH_2	0.6744	0.54	0	0	0	61.13	61.13	76.5	76.5	986.5	697.2
3	1	CH	0.4469	0.228	0	0	0	61.13	61.13	76.5	76.5	986.5	697.2
9	3	ACH	0.5313	0.4	-11.12	-11.12	-11.12	0	0	167	167	636.1	637.3
10	3	AC	0.3652	0.12	-11.12	-11.12	-11.12	0	0	167	167	636.1	637.3
11	4	$ACCH_3$	1.2663	0.968	-69.7	-69.7	-69.7	-146.8	-146.8	0	0	803.2	603.2
12	4	$ACCH_2$	1.0396	0.66	-69.7	-69.7	-69.7	-146.8	-146.8	0	0	803.2	603.2
14	5	OH	1	1.2	156.4	156.4	156.4	89.6	89.6	25.82	25.82	0	-137.1
15	6	CH_3OH	1.4311	1.432	16.51	16.51	16.51	-50	-50	-44.5	-44.5	249.1	0
16	7	H_2O	0.92	1.4	300	300	300	362.3	362.3	377.6	377.6	-229.1	289.6
17	8	ACOH	0.8952	0.68	275.8	275.8	275.8	25.34	25.34	244.2	244.2	-451.6	-265.2
18	9	CH_3CO	1.6724	1.488	26.76	26.76	26.76	140.1	140.1	365.8	365.8	164.5	108.7
20	10	CHO	0.998	0.948	505.7	505.7	505.7	23.39	23.39	106	106	529	-340.2
21	11	CH_3COO	1.9031	1.728	114.8	114.8	114.8	85.84	85.84	-170	-170	245.4	249.6
29	14	CH_2NH_2	1.3692	1.236	-30.48	-30.48	-30.48	-44.85	-44.85	296.4	296.4	-242.8	-481.7
36	17	$ACNH_2$	1.06	0.816	1139	1139	1139	247.5	247.5	762.8	762.8	-17.4	-118.1
42	20	COOH	1.3013	1.224	315.3	315.3	315.3	62.32	62.32	89.96	89.96	-151	339.8
49	22	CCL_2	1.8016	1.448	34.1	34.1	34.1	121.3	121.3	140.8	140.8	527.6	669.9
51	23	CCL_3	2.6401	2.184	36.7	36.7	36.7	228.5	228.5	69.9	69.9	742.1	649.1
99	46	$CON(CH_{2)2}$	2.4054	1.812	27.97	27.97	27.97	0	0	0	0	394.8	0
4	1	C	0.2195	0	0	0	0	61.13	61.13	76.5	76.5	986.5	697.2

Table B.4.3 Interaction parameters (a_{nm}).

Main Group	7	8	9	10	11	14	17	20	22	23	46	1	
	H_2O	ACOH	CH_3CO	CHO	CH_3COO	CH_2NH_2	$ACNH_2$	COOH	CCL_2	CCL_3	$CON(CH_2)_2$	C	
1	1318	1333	476.4	677	232.1	391.5	920.7	663.5	53.76	24.9	380.9	0	CH_3
1	1318	1333	476.4	677	232.1	391.5	920.7	663.5	53.76	24.9	380.9	0	CH_2
1	1318	1333	476.4	677	232.1	391.5	920.7	663.5	53.76	24.9	380.9	0	CH
3	903.8	1329	25.77	347.3	5.994	161.7	648.2	537.4	-144.4	-231.9	0	-11.12	ACH
3	903.8	1329	25.77	347.3	5.994	161.7	648.2	537.4	-144.4	-231.9	0	-11.12	AC
4	5695	884.9	-52.1	586.6	5688	19.02	664.2	872.3	-111	-80.25	0	-69.7	$ACCH_3$
4	5695	884.9	-52.1	586.6	5688	19.02	664.2	872.3	-111	-80.25	0	-69.7	$ACCH_2$
5	353.5	-259.7	84	-203.6	101.1	8.642	-52.39	199	65.28	-98.12	-382.7	156.4	OH
6	-181	-101.7	23.39	306.4	-10.72	359.3	489.7	-202	-102.5	-139.4	0	16.51	CH_3OH
7	0	324.5	-195.4	-116	72.87	48.89	243.2	-14.09	370.4	353.7	835.6	300	H_2O
8	-601.8	0	-356.1	-271.1	-449.4	0	119.9	408.9	0	0	0	275.8	ACOH
9	472.5	-133.1	0	-37.36	-213.7	0	6201	669.4	-130.3	-354.6	0	26.76	CH_3CO
10	480.8	-155.6	128	0	-110.3	0	0	497.5	67.52	-483.7	0	505.7	CHO
11	200.8	-36.72	372.2	185.1	0	0	475.5	660.2	108.9	-209.7	0	114.8	CH_3COO
14	-330.4	0	0	0	0	0	-200.7	0	0	0	0	-30.48	CH_2NH_2
17	-341.6	-253.1	-450.3	0	-294.8	-15.07	0	-396	-111	0	0	1139	$ACNH_2$
20	-66.17	-11	-297.8	-165.5	-256.3	0	493.8	0	-44.7	39.63	-322.3	315.3	COOH
22	708.7	0	82.86	190.6	-133	0	140.8	543.3	0	0	0	34.1	CCL_2
23	826.8	0	552.1	242.8	176.5	0	0	504.2	-84.53	0	0	36.7	CCL_3
46	-509.3	0	0	0	0	0	0	-70.25	0	0	0	27.97	$CON(CH_2)_2$
1	1318	1333	476.4	677	232.1	391.5	920.7	663.5	53.76	24.9	380.9	0	C

From equation (28), the Matrix of Ψ_{nm} is calculated as follows:

$$\Psi_{nm} = \exp\left(-\frac{a_{nm}}{T}\right)$$

Table B.4.4 Matrix of Ψ_{nm} values at 130°C

	CH_3	CH_2	CH	ACH	AC	$ACCH_3$	$ACCH_2$	OH	CH_3OH	H_2O	ACOH
CH_3	1	1	1	0.8593054	0.8593054	0.8271612	0.8271612	0.0865546	0.1773942	0.0380348	0.0366456
CH_2	1	1	1	0.8593054	0.8593054	0.8271612	0.8271612	0.0865546	0.1773942	0.0380348	0.0366456
CH	1	1	1	0.8593054	0.8593054	0.8271612	0.8271612	0.0865546	0.1773942	0.0380348	0.0366456
ACH	1.0279667	1.0279667	1.0279667	1	1	0.6608437	0.6608437	0.2064237	0.2058101	0.1062622	0.037011
AC	1.0279667	1.0279667	1.0279667	1	1	0.6608437	0.6608437	0.2064237	0.2058101	0.1062622	0.037011
$ACCH_3$	1.1887336	1.1887336	1.1887336	1.4392648	1.4392648	1	1	0.1363799	0.2239758	7.329E-07	0.1113625
$ACCH_2$	1.1887336	1.1887336	1.1887336	1.4392648	1.4392648	1	1	0.1363799	0.2239758	7.329E-07	0.1113625
OH	0.6784497	0.6784497	0.6784497	0.8007153	0.8007153	0.9379622	0.9379622	1	1.4050487	0.4160937	1.9044192
CH_3OH	0.9598747	0.9598747	0.9598747	1.1320423	1.1320423	1.1167032	1.1167032	0.5390838	1	1.5666889	1.286935
H_2O	0.4751428	0.4751428	0.4751428	0.4071096	0.4071096	0.3919488	0.3919488	1.7652191	0.4875594	1	0.4471276
ACOH	0.5045378	0.5045378	0.5045378	0.9390796	0.9390796	0.545676	0.545676	3.0654016	1.9305784	4.4492905	1
CH_3CO	0.9357777	0.9357777	0.9357777	0.7064426	0.7064426	0.4035905	0.4035905	0.6649545	0.7636645	0.3097405	1.3911769
CHO	0.285255	0.285255	0.285255	0.9436329	0.9436329	0.7687961	0.7687961	0.2692361	2.325313	0.3034288	1.4710267
CH_3COO	0.7521966	0.7521966	0.7521966	0.8082182	0.8082182	1.5245195	1.5245195	0.5440542	0.5384157	0.6076978	1.0953596
CH_2NH_2	1.0785361	1.0785361	1.0785361	1.1176731	1.1176731	0.4794047	0.4794047	1.8262364	3.3030313	2.2694694	1
$ACNH_2$	0.0592938	0.0592938	0.0592938	0.5412276	0.5412276	0.1507549	0.1507549	1.0441051	1.3403665	2.333402	1.8734957
COOH	0.4574485	0.4574485	0.4574485	0.8567727	0.8567727	0.8000006	0.8000006	1.4543374	0.4304765	1.1783704	1.0276608
CCL_2	0.9188946	0.9188946	0.9188946	0.7401662	0.7401662	0.705217	0.705217	0.2701727	0.1898228	0.1724054	1
CCL_3	0.9129875	0.9129875	0.9129875	0.5673456	0.5673456	0.8408142	0.8408142	0.1586977	0.1998735	0.1286256	1
$CON(CH_2)_2$	0.9329733	0.9329733	0.9329733	1	1	1	1	0.3755784	1	3.5370799	1
C	1	1	1	0.8593054	0.8593054	0.8271612	0.8271612	0.0865546	0.1773942	0.0380348	0.0366456

Table B.4.4 Matrix of Ψ_{nm} values at 130°C

	CH_3CO	CHO	CH_3COO	CH_2NH_2	$ACNH_2$	COOH	CCL_2	CCL_3	$CON(CH_2)_2$	C
CH_3	0.3067586	0.186509	0.562302	0.3786653	0.1018998	0.1928603	0.8751588	0.9401051	0.3887536	1
CH_2	0.3067586	0.186509	0.562302	0.3786653	0.1018998	0.1928603	0.8751588	0.9401051	0.3887536	1
CH	0.3067586	0.186509	0.562302	0.3786653	0.1018998	0.1928603	0.8751588	0.9401051	0.3887536	1
ACH	0.9380785	0.4225422	0.9852421	0.6695889	0.2003202	0.2636843	1.4307222	1.7775218	1	1.0279667
AC	0.9380785	0.4225422	0.9852421	0.6695889	0.2003202	0.2636843	1.4307222	1.7775218	1	1.0279667
$ACCH_3$	1.1379544	0.2333907	7.457E-07	0.9539171	0.1925257	0.114898	1.3169675	1.220252	1	1.1887336
$ACCH_2$	1.1379544	0.2333907	7.457E-07	0.9539171	0.1925257	0.114898	1.3169675	1.220252	1	1.1887336
OH	0.8119154	1.6570235	0.7781973	0.9787919	1.1387733	0.6104171	0.8505051	1.2755575	2.5838343	0.6784497
CH_3OH	0.9436329	0.4676595	1.0269473	0.4101503	0.2968037	1.6504603	1.2894913	1.4130875	1	0.9598747
H_2O	1.6236604	1.3334027	0.8346427	0.8857948	0.5470312	1.0355677	0.3990116	0.4158873	0.1258484	0.4751428
ACOH	2.4188544	1.9590397	3.0487192	1	0.742741	0.3626697	1	1	1	0.5045378
CH_3CO	1	1.0970999	1.6990608	1	2.089E-07	0.1900583	1.3815482	2.4098713	1	0.9357777
CHO	0.7279669	1	1.3146828	1	1	0.2911164	0.8457926	3.3194582	1	0.285255
CH_3COO	0.3972341	0.6318304	1	1	0.3074442	0.1944454	0.7632858	1.6822863	1	0.7521966
CH_2NH_2	1	1	1	1	1.6451468	1	1	1	1	1.0785361
$ACNH_2$	3.0555328	1	2.0776584	1.0380881	1	2.6704972	1.3169675	1	1	0.0592938
COOH	2.0931767	1.5075973	1.8884257	1	0.2938005	1	1.1172573	0.9063762	2.2243268	0.4574485
CCL_2	0.8142145	0.6232691	1.3908319	1	0.705217	0.2598535	1	1	1	0.9188946
CCL_3	0.2542428	0.5475742	0.6454534	1	1	0.2863183	1.2332757	1	1	0.9129875
$CON(CH_2)_2$	1	1	1	1	1	1.1903564	1	1	1	0.9329733
C	0.3067586	0.186509	0.562302	0.3786653	0.1018998	0.1928603	0.8751588	0.9401051	0.3887536	1

Table B.4.5 Component Structure Information and Activity Coefficient Calculation at 130°C

SubGroup		Limonene	Water	Sabinene	Other	$\sum_j v_k^{(i)} x_j$
	x_i	0.409	0.001	0.427	0.167	
	γ	1.010	244.752	1.028	1.018	
1	CH3	1		2	2	1.596867858
2	CH2	4		4	2	3.676345377
3	CH			2		0.853063577
9	ACH	2			3	1.320108746
10	AC				1	0.167499817
11	ACCH3	1			1	0.576304465
12	ACCH2					0
14	OH					0
15	CH3OH					0
16	H2O		1			0.001093665
17	ACOH					0
18	CH3CO					0
20	CHO					0
21	CH3COO					0
29	CH2NH2					0
36	ACNH2					0
42	COOH					0
49	CCL2					0
51	CCL3					0
99	CON(CH2)2					0
4	C	1		2	1	1.429368041
$\sum_n v_k^{(i)} x_j$		3.679241827	0.001093665	4.265317883	1.674998171	9.620651547
N groups		9	1	10	10	

Table B.4.6 Area fraction (Θ) and mole fraction values at 130°C

	X_i					Θ				
	Limonene	Water	Sabinene	Other	Mix	Limonene	Water	Sabinene	Other	Mix
CH3	0.111111111	0	0.2	0.2	0.165983338	0.177554439	0.291752944	0.291752944	0.291752944	0.291752944
CH2	0.444444444	0	0.4	0.2	0.382130603	0.452261307	0.427720908	0.427720908	0.427720908	0.427720908
CH	0	0	0.2	0	0.088670042	0	0.041905079	0.041905079	0.041905079	0.041905079
ACH	0.222222222	0	0	0.3	0.137216148	0.167504188	0.113767998	0.113767998	0.113767998	0.113767998
AC	0	0	0	0.1	0.017410444	0	0.004330579	0.004330579	0.004330579	0.004330579
ACCH3	0.111111111	0	0	0.1	0.059902852	0.202680067	0.120192607	0.120192607	0.120192607	0.120192607
ACCH2	0	0	0	0	0	0	0	0	0	0
OH	0	0	0	0	0	0	0	0	0	0
CH3OH	0	0	0	0	0	0	0	0	0	0
H2O	0	1	0	0	0.000113679	0	0.000329885	0.000329885	0.000329885	0.000329885
ACOH	0	0	0	0	0	0	0	0	0	0
CH3CO	0	0	0	0	0	0	0	0	0	0
CHO	0	0	0	0	0	0	0	0	0	0
CH3COO	0	0	0	0	0	0	0	0	0	0
CH2NH2	0	0	0	0	0	0	0	0	0	0
ACNH2	0	0	0	0	0	0	0	0	0	0
COOH	0	0	0	0	0	0	0	0	0	0
CCL2	0	0	0	0	0	0	0	0	0	0
CCL3	0	0	0	0	0	0	0	0	0	0
CON(CH2)2	0	0	0	0	0	0	0	0	0	0
C	0.111111111	0	0.2	0.1	0.148572894	0	0	0	0	0
$\sum_n Q_n X_n$	0.530666667	1.4	0.4312	0.5064	0.48244199					

Table B.4.7 Parameter to calculate group activity coefficient at 130°C

	$\sum_n \Theta_n \Psi_{nm}$					$\frac{\Theta_m}{\sum_n \Theta_n \Psi_{nm}}$				
	Limonene	Water	Sabinene	Other	Mix	Limonene	Water	Sabinene	Other	Mix
CH3	1.042937072	0.475142795	1	1.043366932	1.025814065	0.170244633	0	0.393320965	0.320992646	0.284411136
CH2	1.042937072	0.475142795	1	1.043366932	1.025814065	0.433641989	0	0.500927644	0.204405694	0.416957539
CH	1.042937072	0.475142795	1	1.043366932	1.025814065	0	0	0.105751391	0	0.04085056
ACH	1.000418545	0.407109556	0.859305386	1.006840466	0.945478886	0.167434109	0	0	0.235356874	0.120328438
AC	1.000418545	0.407109556	0.859305386	1.006840466	0.945478886	0	0	0	0.023535687	0.004580303
ACCH3	0.834333311	0.39194879	0.827161206	0.816847006	0.828149724	0.242924577	0	0	0.234013514	0.14513391
ACCH2	0.834333311	0.39194879	0.827161206	0.816847006	0.828149724	0	0	0	0	0
OH	0.116731764	1.76521913	0.086554584	0.127324357	0.107253358	0	0	0	0	0
CH3OH	0.191595125	0.487559449	0.177394161	0.1937054	0.186451135	0	0	0	0	0
H2O	0.04175441	1	0.038034767	0.048548845	0.04183826	0	1	0	0	0.007884774
ACOH	0.051850441	0.447127575	0.036645611	0.051023233	0.045804594	0	0	0	0	0
CH3CO	0.580974159	1.623660422	0.3067586	0.630206442	0.481654606	0	0	0	0	0
CHO	0.235547538	1.333402697	0.186509015	0.256995832	0.220397369	0	0	0	0	0
CH3COO	0.519178967	0.834642674	0.562301984	0.565061327	0.544755995	0	0	0	0	0
CH2NH2	0.543988297	0.885794764	0.378665304	0.564459708	0.482331273	0	0	0	0	0
ACNH2	0.136753683	0.547031216	0.101899795	0.14487783	0.124562507	0	0	0	0	0
COOH	0.188922184	1.035567692	0.192860257	0.196418765	0.192131986	0	0	0	0	0
CCL2	1.057763844	0.399011625	0.875158847	1.104427093	0.993715149	0	0	0	0	0
CCL3	1.137156096	0.415887312	0.940105091	1.21194006	1.072501471	0	0	0	0	0
CON(CH2)2	0.615027376	0.125848351	0.388753573	0.664924945	0.53432148	0	0	0	0	0
C	1.042937072	0.475142795	1	1.043366932	1.025814065	0	0	0	0	0

Table B.4.7 Parameter to calculate group activity coefficient at 130°C

	$\sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}}$					$ln\Gamma_k$				
	Limonene	Water	Sabinene	Other	Mix	Limonene	Water	Sabinene	Other	Mix
CH3	0.94870144	0.038034767	1	0.941433014	0.969903024	0.007850546	1.446777151	0	0.01366473	0.003909678
CH2	0.94870144	0.038034767	1	0.941433014	0.969903024	0.004999169	0.921296771	0	0.008701597	0.002489653
CH	0.94870144	0.038034767	1	0.941433014	0.969903024	0.00211076	0.38899197	0	0.003674007	0.001051187
ACH	0.948744639	0.10626222	1.027966712	0.95363093	0.984634096	0.020334761	0.716964292	0.049465678	0.015820757	0.02857185
AC	0.948744639	0.10626222	1.027966712	0.95363093	0.984634096	0.006100428	0.215089288	0.014839703	0.004746227	0.008571555
ACCH3	1.201766897	7.32901E-07	1.188733558	1.231187114	1.207211586	-0.019983967	1.874651405	0.000989409	-0.027959372	-0.018053463
ACCH2	1.201766897	7.32901E-07	1.188733558	1.231187114	1.207211586	-0.013625432	1.278171413	0.000674597	-0.019063208	-0.012309179
OH	0.771627826	0.416093682	0.678449702	0.78325142	0.742985687	2.851498518	0.018757779	3.322236396	2.733319245	2.987490866
CH3OH	1.04047264	1.56668889	0.959874724	1.058717543	1.028263943	2.308238246	0.217168754	2.533933165	2.266425381	2.36469331
H2O	0.450310398	1	0.475142795	0.446758186	0.468281498	5.215895716	0	5.311756554	5.009797356	5.187927555
ACOH	0.59447567	4.449290459	0.504537751	0.635899583	0.606054617	2.288142995	-1.798177812	2.585308227	2.270910741	2.364575066
CH3CO	0.781428297	0.309740528	0.935777748	0.768994435	0.843809998	1.133291606	0.305897612	1.853923618	1.030757528	1.319436396
CHO	0.517017475	0.303428825	0.285254983	0.574080711	0.443560586	1.828526148	0.387577553	2.269531643	1.691814735	1.961186898
CH3COO	0.959908018	0.607697752	0.752196614	0.961202693	0.885299345	1.201994394	0.990237017	1.423041904	1.053420454	1.247819825
CH2NH2	0.954909265	2.269469434	1.078536051	0.968205468	1.027589467	0.808242994	-1.419174502	1.103212214	0.746149477	0.867096821
ACNH2	0.163048747	2.333402021	0.059293763	0.206551332	0.151891028	2.306444531	-0.59580453	2.631168813	2.223855498	2.391742185
COOH	0.614039797	1.178370388	0.457448471	0.649365699	0.571943854	2.512113456	-0.261103874	2.678529308	2.421244149	2.54301773
CCL2	0.850151745	0.172405419	0.918894555	0.839439509	0.878184723	0.135664795	2.528728279	0.310531295	0.088666483	0.185517704
CCL3	0.850588366	0.128625582	0.912987478	0.823325554	0.87154813	0.045604413	3.819194342	0.324927077	-0.033956798	0.127672548
CON(CH2)2	0.973768811	3.537079903	0.932973349	0.983088725	0.990402492	0.928323274	-0.841496859	1.83344733	0.770086202	1.153075455
C	0.94870144	0.038034767	1	0.941433014	0.969903024	0	0	0	0	0

Table B.4.8 Parameter to calculate activity coefficient at 130°C

Substance	Limonene	Water	Sabinene	Others (alpha-pinene)
q_i	4.7760	1.4000	4.3120	5.0640
r_i	6.1471	0.9200	5.8326	6.5959
θ_i	0.4207	0.0003	0.3963	0.1828
$\emptyset_i$	0.4115	0.0002	0.4074	0.1809
$ln\gamma_i^{comb}$	0.0057	0.3123	0.0073	-0.0018
$ln\gamma_i^{res(i)}$	0.0485	0.0000	0.0000	0.0690
$ln\gamma_i^{res}$	0.0530	5.1879	0.0199	0.0890

To obtain the activity coefficient for each substance, a trial value of xi was performed from Table B.4.5, which resulted in a pressure of 760 mmHg. This value was then substituted in the modified Raoult's law, and the vapor fraction was found using the Antoine equation to calculate the vapor pressure of each substance.

Table B.4.9 Modified Raoult's law parameters and Antoine coefficients at 130°C.

	Limonene	Water	Sabinene	Others (alpha-pinene)
A	7.06744	8.14019	-	7.06153
B	1691.15	1810.94	-	1621.22
C	227.441	244.485	-	231.645
P_i^{sat}[mmHg]	216.855112	2015.466024	148.64	378.9880307
y_i	0.11801	0.71094	0.08585	0.08520
$y_{i(EO)}$	0.408262913	-	0.297000003	0.294737084

Example for calculated activity coefficient of limonene at 130 °C

Table. 4.10 Matrix of Ψ_{nm} values of limonene at 130°C

Ψ_{nm}	CH3	CH2	ACH	ACCH3	C
CH3	1	1	0.85931	0.82716	1
CH2	1	1	0.85931	0.82716	1
ACH	1.02797	1.02797	1	0.66084	1.02797
ACCH3	1.18873	1.18873	1.43926	1	1.18873
C	1	1	0.85931	0.82716	1

Table B.4.11 Parameter to calculate combinatorial part of limonene at 130°C

SubGroup	V_k	X_m	Q_m	Θ_m	$\sum_n \Theta_n \Psi_{nm}$	$ln\Gamma_k$	$ln\Gamma_k^{(1)}$	$ln\gamma_i^{res}$
CH3	1	0.11	0.848	0.18	1.04	0.00391	0.00785	0.0045
CH2	4	0.44	0.54	0.45	1.04	0.00249	0.00500	
ACH	2	0.22	0.4	0.17	1.00	0.02857	0.02033	
ACCH3	1	0.11	0.968	0.20	0.83	-0.01805	-0.01998	
C	1	0.11	0	0.00	1.04	0.00000	0.00000	
$\sum_n j$	9	$\sum_n Q_n X_n$	0.53		$\sum_k v_k^{(i)} ln\Gamma_k$	0.0485	0.0530	

Table B.4.12 Parameter to calculate residual part of limonene at 130°C

SubGroup	V_k	R_k	Q_k	r_i	q_i	$\emptyset_i$	θ_i	$ln\gamma_i^{comb}$
CH3	1	0.9011	0.848	0.9011	0.848	0.4207	0.4115	0.0057
CH2	4	0.6744	0.54	2.6976	2.16			
ACH	2	0.5313	0.4	1.0626	0.8			
ACCH3	1	1.2663	0.968	1.2663	0.968			
C	1	0.2195	0	0.2195	0			

From equation (17), the activity coefficient is calculated as follows:

$$\gamma_{limonene} = EXP(0.0057 + 0.045)$$

$$\gamma_{limonene} = 1.010$$

And from modified Raoult's law equation based on ideal gas assumption, the vapor fraction is calculated as follows:

$$y_{limonene} = (0.409x1.010 + 216.855\ mmHg)/760\ mmHg$$

$$y_{limonene} = 0.11801$$

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