Mathematical Modelling Of Extraction Of Oil From *Aquilaria Malacenssis* Wood Employing Subcritical Conditions

Zurina Zainal Abidin*, Mahtab Samadi, Dayang Radiah Awang Biak, and Robiah Yunus

Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

* Corresponding author. E-mail: zurina@upm.edu.my

Subcritical water extraction (SWE) is gaining popularity due to its ability to manipulate water properties at high pressure and temperature. Here, the essential oil from *Aquilaria Malacenssis* wood was recovered using the subcritical technique. The aim is to elucidate SWE mechanism or behaviour and mathematically define the process kinetics for future scaling up, designing unit operation and improving efficiency. The extraction processes were carried out at various subcritical conditions such as varying temperature and time. These concentration-time profile data were analyzed using four models namely partitioning coefficient, one-site desorption, two-site desorption and thermodynamic partition with external mass transfer. Concentration (yield)-time profile indicated that the subcritical water extraction occurred in two simultaneous processes of fast and slow desorption. The fast process persisted during the initial 10 minutes with large changes in the essential oil yield. From this onwards until the end of extraction time, a gradual slow increment was seen till a plateau was reached. Three models which are second order, two-site kinetic and partitioning coefficient with external mass transfer were found to give reasonable SSR and R^2 values. However, the two-site kinetic/second order model emerged to best fit the experimental data with low SSR of less than 0.002 and high R^2 of greater than 0.99. Using the two rate constants of k_1 and k_2 from the two-site kinetic model, activation energies were calculated and found to be 16.5 KJ/mol and 28 KJ/mol for fast desorption and slow diffusion respectively. In short, SWE has demonstrated good enhancement of the extraction yield and temperature being the critical parameter. These findings on kinetics and modelling can facilitate the reduction of energy and time for scaling up and optimization.

Keywords: Gaharu, *Aquilaria Malacenssis*, Subcritical, Kinetics, Essential Oil

1. Introduction

Essential oil is the odoriferous organic compounds that give specific aroma and flavor to particular plants [1, 2]. It comprises of complex mixture of low molecular weight compounds synthesized in different plant organs as the secondary metabolites They typically accumulated in secretory cells such as oil glands, trichomes (glandular hairs), oil ducts, and resin ducts of the particular part of plants like flowers, fruits, bark, wood, seeds, and roots [1–3].

Aquilaria malaccensis essential oil, often referred to as agarwood oil or oud oil, is a luxurious and highly coveted aromatic substance derived from the resinous heartwood of the *Aquilaria malaccensis* tree. For centuries, the oil extracted from the resin has been treasured for its intricate and enchanting scent, making it a prized ingredient in the fragrance and perfume industry, as well as in traditional medicine and spiritual practices [4]. Among re-

ported bioactivities of *Aquilaria Malaccensis* EO are antibacterial or antimicrobial, antioxidant, anticancer, antifungal, anti-inflammatory, and insecticidal [2, 5, 6]. This makes *A. Malaccensis* EO expensive and a litre of high-quality agarwood oils can cost from USD 30,000 to USD 50,000, depending on the oil purity, fragrance strength, longevity, resin content and geographical origin. This indirectly demands an effective technique for extracting valuable *A. Malaccensis* EO.

The production of *Aquilaria malaccensis* EO is a labor-intensive and intricate process that involves skilled artisans and a deep understanding of the agarwood formation. Among the two common but very time-consuming practices famously adopted by industries in obtaining essential oil from *Aquilaria malaccensis* wood are hydrodistillation and steam distillation [7–9]. Typical hydrodistillation and steam distillation require one week soaking of the wood prior to extraction [10, 11] and this is followed by additional 16 hours to recover the oil from the *A.malaccensis* wood. These extensive processes in hydrodistillation and steam distillation eventually lead to inefficient processes with large energy consumption, loss of volatile compounds and biodegradation of unsaturated compounds [12]. To tackle these downsides, alternative extraction techniques have been utilized.

Subcritical water extraction (SWE) is gaining increasing attention as a sustainable and efficient method for obtaining essential oils from plant materials [13]. SWE utilizes water under controlled high temperature and pressure conditions, typically within the subcritical range (100 °C to 374 °C). This innovative approach harnesses the unique properties of water being liquid at these conditions, allowing it to act as a selective and effective solvent for extracting essential oils from various botanical sources [14]. The basic principles originate from the fact that water is a molecule with dipole moments, that forms hydrogen bonds intermolecularly. Principally, at an increasing temperature and pressure, either approaching or exceeding the water's critical point, several physicochemical properties of water such as density, viscosity, permittivity (dielectric constant), and surface tension of water are decreasing, while the diffusivity is increased accordingly [15–17]. The properties' changes are attributed to the disruption of intermolecular forces due to the thermal energy received from heating. Thus, liquid water expands upon heating at saturation pressure, lowering down the surface tension and leading to an increase of vapor density, which then results in a decrease of liquid density and viscosity [18, 19]. The decline in density and viscosity of water, enhance the mobility of ions and increase the diffusivity characteristic [19]. An increase in water diffusivity can improve the rate of solute-solvent mass transfer [20].

One of the remarkable features of SWE is its ability to capture a broader spectrum of compounds from plants compared to conventional steam distillation or solvent-based extractions. It has been employed for extraction of bioactive compounds [21, 22], waste [23], oil, essential oil [13] and many others. Since water's properties change with temperature and pressure, SWE can be fine-tuned to selectively extract specific constituents from plants, preserving the intricate chemical profiles of essential oils. This precision in extraction enables the capture of not only the characteristic aroma compounds but also potentially valuable secondary metabolites with potential therapeutic or industrial applications. SWE has also successfully produced larger yield and better quality of essential oil using small amount of raw material in a substantially lesser extraction time (two to three times) [24].

Furthermore, SWE aligns with the growing global demand for sustainable and eco-friendly extraction methods. It minimizes the use of organic solvents, reducing both environmental impact and potential health risks for operators. Additionally, the reduced extraction times and energy consumption associated with SWE contribute to its environmental benefits. As the interest in natural products and essential oils continues to rise, subcritical water extraction stands out as a promising and green technology that combines efficiency, selectivity, and environmental responsibility in the extraction of essential oils from plants. Extraction of essential oil from *Aquilaria Crassna* using SWE has been successfully demonstrated by Yoswathana et al. [8] in a shorter time and gave better quality. This is followed by Samadi et al. [25] who also investigated the use of SWE for recovering essential oil from *Aquilaria Malacenssis*. The researchers optimized the extraction process using response surface methodology and concluded that 225 °C and 17 mins were the best operating conditions. The kinetics modelling of the process pertaining to SWE of *A.Malacenssis* wood has yet to be reported.

Mathematical modelling is crucial for process optimization, designing and production of essential oils at larger scale. Typical empirical modelling approaches using software like Response Surface Methodology are good in optimization and understanding the correlations between process variables. In most cases of extraction, the models reported are the quadratic polynomial equations that are applied to decide the best combination of the operating parameters. Therefore, the applicability of this model is limited by the predetermined experimental range of the studied variables which only represents the effect of the

studied variable on the analysed response without understanding the underlying mechanism and fundamentals of the process [26, 27]. Due to this reason, mathematical models describing the kinetic, mass transfer, and thermodynamic behaviours of the extraction process are also examined to fill this gap. Several models have been reported for modelling SWE including thermodynamic based model, synthetic models, kinetic absorption-based model, thermodynamic separation with external mass transfer resistance model and differential mass balance based model [28].

Thermodynamic model describes a simple model based on thermodynamic distribution coefficient, k_D (ratio of solute concentration in matrix to solute concentration in extraction fluid). Here, the initial desorption step and the separation of the lattice fluid are assumed fast and have no significant effect on the extraction rate. Next under kinetic absorption models, there are the single-location or one-site kinetic desorption model and the two-dimensional or two-site kinetic desorption model. One-site kinetic desorption model or the pseudo-first-order model is based on the mass transfer model of Fick's second law where the extraction is controlled by intra-particle diffusion to yield an exponential extraction curve. The two-site kinetic model meanwhile is a modification of one-site desorption model. It is a two-stages extraction involving the washing stage, referring to the fast rate desorption of analyte from the broken cells, and the diffusion stage, referring to the slow rate desorption of analyte from the intact cells [29]. Another model is the second-order rate law that assume that the extraction process consists of two mechanisms, involving intense dissolution of compounds at the beginning of extraction followed by a much weaker extraction due to the external diffusion [30, 31].

The next model is thermodynamic with external mass transfer resistance model where in this case external mass transfer predominantly controls the extraction. The extraction is governed by external mass transfer coefficient (k_e) and partitioning equilibrium factor (k_D). The last model considered for SWE is differential mass balance equation and is claimed to be the most comprehensive among all models [23]. Here, a volumetric element with finite difference in height of a cylindrical extraction bed is selected and mass balance is performed on it.

A synthetic model (SM) on the other hand, is created using self-contained software components that operate independently of the model they constitute. These components are systematically integrated to produce a unified entity. When an SM is executed as a simulation, it manifests the model's behavior in accordance with a predetermined computational blueprint.

A number of proposed models have been applied to SWE essential oil recovery on abundant agricultural materials. In the SWE of essential oil from *Zataria multiflora Boiss*, Khajenoori et al. [32] applied all models except for second order to explain the kinetics of the process and they concluded that mathematical model based on the combination of partition coefficient (k_D) and external mass transfer fitted well to the experimental results. Another study on the SWE extraction of citrus flavonoids found that the two-site kinetic desorption model fitted the entire extraction period very well, suggesting that the extraction was mainly controlled by intra-particle diffusion [33]. Duba et al. [34] also found that the two-site kinetic models fitted remarkably well with experimental data with root mean square error in the range of 10^{-2}-10^{-1} and average absolute relative deviation of 0.5–4%. Their work focused on extracting polyphenols from grape skins and defatted grape seeds (cultivar: *Pinot Nero*) using subcritical water in a semi-continuous mode. In addition, Islam et al. [35] used four models (all mentioned above except second order) to describe the SWE of polycyclic aromatic hydrocarbons and two-site kinetic model was also found to best described phenanthrene, fluoranthene and pyrene. Another investigation on subcritical extraction of essential oil from *A. Malaccensis* leaves meanwhile concluded that the second order model being the best model for describing the SWE process [36]. In the extraction of castor oil by SWE, a team of researchers found that the process can be described by what they called as irreversible consecutive unimolecular-type first order mechanism which is similar to two-site kinetic model [13]. As for synthetic modelling, so far to our knowledge, no SWE modelling has been reported.

All these studies related to modelling of SWE process in extracting bioactive compounds from plant materials shows diversity in the best model that fits for various extraction process from different plant parts. The SWE extraction controlling mechanism may differ in various instruments, samples, and conditions. For instance, some bioactive compounds are extracted from the leave part, while others are extracted from the skins, peels, seeds and others. The bioactive compounds could be residing in various locations in the plant matrix being it in the cytoplasm, vacuoles, cell wall, organelles and others that may have various resistance and thus affect the ease of extraction.

In this current work, the kinetics and thermodynamics of the SWE of *Aquilaria Malaccensis* EO will be investigated and presented. The modelling studies were performed by fitting the experimental data in various models including thermo-dynamic partition model, one-site kinetic desorption model, second order, two-site kinetic desorption model

and thermodynamic partitioning with external mass transfer resistance model. The thermodynamic parameters of the extraction process including the Arrhenius equation was determined. This study is significantly important to elucidate necessary information for precise controlling, better optimizing and enhance efficiency of the SWE process particularly for *Aquilaria Malaccensis* [37].

2. Theory and formula

In SWE, six steps are known to take place, i) rapid entry of fluid into matrix, ii) desorption of solute from active matrix, iii) penetration of solute through organic matter, iv) penetration of analytes into stationary fluids in porous material, v) desorption of analytes into layer enveloping the solid materials and vi) washing of solutes with moving fluid by thermodynamics. In modelling Subcritical Water Extraction (SWE) of bioactive compounds from plant material, only three main steps are considered which are transfer of compound within plant matrix (internal penetration), external penetration through film layer enveloping the solid plant material and washing solutes with solvents. Hence, several mathematical models are used such as one-site kinetic model, two-site kinetic model, second order, thermodynamic with external mass transfer partitioning model [28, 32, 38, 39]. External mass transfer model plus partitioning coefficient stems from the concentration gradient between adsorbed solid and liquid phases (solute desorption) which are dominant in the second and fourth steps of subcritical mechanism. However, desorption of both one-site and two-site models presumed distinct interactions between chemicals and specialized adsorption [35]. Each of the models will be discussed in detail next.

2.1. One-site kinetic desorption model

Generally, one-site kinetic desorption is expressed using simple first order kinetic model and is governed by intra-particle diffusion [28, 32, 35, 40]. This model assumes chemical compounds to be uniformly dispersed throughout the matrix and at the beginning of the extraction, the concentration of chemical compounds in the matrix surface is considered as zero (infinite solubility). Hence, one-site kinetic desorption model for a uniform spherical matrix is defined as Eq. (1) [28, 32, 35, 40].

$$\frac{c_r}{c_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D_e n^2 \pi^2 t}{r^2}\right) \tag{1}$$

Where C_r is the solution for the ratio of the mass of the substance which stays in the matrix, t is the time of extraction, C_0 is the initial mass of extractable substance, n is an integer, D_e is the effective diffusion coefficient of the

substances in the solid sphere (m^2/s) and r is the radius of sphere.

$$\ln\left(\frac{c_r}{c_0}\right) = -0.4977 - \frac{t}{t_0} \tag{2}$$

Eq. (2) is linear form of Eq. (1). In practice, the y-intercept value changes with the size distribution, particle shape, and the distribution of solute within the matrix (near surface or in the interior). Eq. (2) can be rewritten as ratio of solute mass removed after time t to the initial mass, C_0 as below:

$$\frac{C_t}{C_0} = 1 - e^{-k_1 t} \tag{3}$$

where C_t is the mass of the solute isolated by the solvent after time t (mg/g), C_0 is the initial mass of solute in the matrix (mg/g), C_t/C_0 is the portion of the extracted solute after time t and k_1 is the first order rate constant.

The fitting of experimental data to this first order model is generally done by plotting a linear graph of ln C_t/C_0 versus time and the constant k_1 can be found from the slope.

2.2. Second order model

The second order model also known as pseudo second order, describes an extraction mechanism that occurs in two simultaneous processes. Similarly, to the first order model, uniform distribution of materials, uniform size of materials, and zero concentration of chemical compounds at the time zero are assumed here. Eq. (1) describes the rate of dissolution of the solute contains in the solid to the solution. The differential equation is as follow [28, 38, 39, 41].

$$\frac{dc_t}{dt} = k_2 \left(c_\infty - c_t\right)^2 \tag{4}$$

Where t is the time of extraction, C_t is the amount of extracted essential oil at time t, C_∞ is the absolute amount of extracted essential oil at infinite time and k_2 is the second order rate constant.

Integrated pseudo-second order kinetic will yield Eq. (5) which was calculated for conditions between $C_t = 0$, $t = 0$ to $C_t = C_t$, $t = t$.

$$c_t = \frac{t c_\infty^2 k_2}{t k_2 c_\infty + 1} \tag{5}$$

Obviously, Eq. (5) can be linearised to various expressions for determination of the constants involved including Eqs. (6) and (7), while 7 being the most common forms.

$$\frac{1}{(C_\infty - C_t)} = \frac{1}{C_\infty} + k_2 t \tag{6}$$

$$\frac{t}{c_t} = \frac{1}{k_2 c_\infty^2} + \frac{1}{c_\infty}t \qquad (7)$$

The slope and intercept of the plot of t/C_t versus time yields the second order rate constant (k_2).

2.3. Two-site kinetic desorption model

Two-site kinetic is a modified form of the one-site kinetic model. It describes the extraction to proceed in both "fast" and "slow" modes [28, 32, 40] and hence additional rate constant (k) were used. Fast process refers to rapid diffusion of the solute residing near the surface or inside cells with damage walls while slow process refers to slow diffusion of solute to the surface of plant substances from intact cells.

In this model, a portion (F) of the substance under analysis rapidly desorbs with a rate constant (k_1), while the remainder portion ($1 - F$) desorbs more slowly with a rate constant (k_2). This model is characterised by two first-order expressions and can be elucidated using the following Eq. (8) [28, 40]:

$$\frac{c_t}{c_0} = 1 - \left[Fe^{-k_1 t}\right] - \left[(1-F)e^{-k_2 t}\right] \qquad (8)$$

where C_t is the mass of analyte extracted after time t (mg/g), C_0 is the initial total mass of the analyte in the matrix (mg/g), F is the portion of the substance under analysis rapidly desorbs, k_1 is the first-order rate constant describing the quickly released fraction i.e. F (min^{-1}) and k_2 is the first-order rate constant describing the slowly released fraction i.e. ($1 - F$) (min^{-1}).

The concentration profile with time will yield a nonlinear trend and the constants (k_1 and k_2) can be determined accordingly from the curve. The two-site kinetic model excludes solvent volume, and only based on the extraction time. Thus, changing the solvent flowrate has no profound effect on extraction efficiency [32, 35].

2.4. Thermodynamic partition with external mass transfer model

This model elucidates the process of extraction governed by external mass transfer, with its rate being characterized by a resistance-type model in the following structure [7, 28].

$$\frac{\partial C_S}{\partial t} = -k_e a_p \left[\left(\frac{c_s}{k_D}\right) - c_1\right] \qquad (9)$$

where C is the fluid phase concentration (mol·m^{-3}), C_s is the solid phase concentration (mol·m^{-3}), t is the time of extraction, k_e is the external mass transfer coefficient (m·min^{-1}), a_p is the specific surface area of particles (m^2·$^{-3}$)

and k_D is the partitioning equilibrium factor (k_D = concentration of solute in matrix/concentration of solute in liquid).

When the solute concentration in the bulk fluid is low, we can express the relationship between the solute concentration in the solid matrix and that in the extraction fluid using a partitioning equilibrium factor k_D. Then Eq. (9) becomes:

$$c_s = c_0 \exp\left(-\frac{k_e a_p t}{k_D}\right) \qquad (10)$$

Eq. (10) can also be restated as the proportion of the diffusing solute's mass exiting the sample to the initial mass of solute in the sample, represented as C_t/C_0, as shown below:

$$\frac{c_t}{c_0} = 1 - \exp\left(-\frac{k_e a_p t}{k_D}\right) \qquad (11)$$

Typically, a_p and k_e are assessed together as a combined parameter called $k_e a_p$ since it is challenging to isolate and measure them individually. It represents the overall volumetric mass transfer coefficient and depends on factors such as size/shape of plant sample and water flow rate through the extractor [32, 35]. The concentration profile against time is normally non-linear and the suitability of this thermodynamics model for describing any extraction process is usually assessed by calculating the values of the constants, k_D and $k_e a_p$. The nature of the curve fit remains the same as the nature of the curve fit for one-site kinetic desorption model with $k_e a_p/k_D$ becomes equivalent to k_1.

2.5. Thermodynamics

Thermodynamic behavior of a system or process could be described by thermodynamic properties or parameters such as equilibrium constant (K), enthalpy change (ΔH), entropy change (ΔS), Gibbs free energy (ΔG), and activation energy (E_a) [42, 43]. Several studies have been done to evaluate the thermodynamic parameters for solvent extraction of plant compounds [44–47]. In this work, the focus will be on calculating the activation energy and the relationship between the rate constant (k) with temperature can be expressed by the Arrhenius equation as shown in Eq. (12).

$$k = Ae^{-\frac{E_a}{RT}} \qquad (12)$$

$$\ln k = -\frac{E_a}{RT} - \ln A \qquad (13)$$

Where A is the pre-exponential constant, R is the the universal gas constant (8.314 J/(mol.K), T is the temperature in a unit Kelvin (K) and E_a is the the activation energy.

The linear relationship between lnk and $1/T$ (Eq. (13)) can be used to estimate the activation energy of the process based on the slope and interception of the curve. From Eq. (12), it can be seen that the larger the ratio of E_a/RT, the smaller the rate constant of reactions exponentially. This means that high temperature and low activation energy favor larger rate constants, and thus speed up the reaction. Since these terms occur in an exponent, their effects on the rate constant are quite substantial. Constant A meanwhile can de expressed as a function of frequency factor and steric factor.

3. Experimental setup

3.1. Wood sample preparation

Wood of *Aquilaria malaccensis* collected from Forest Research Institute Malaysia (FRIM) garden. The wood was allowed to dry naturally in a dark environment, away from both sunlight and temperature-induced volatile losses. It was then kept in a chilled room at 4°C until further used. The preparation of wood started with chopping it into smaller pieces using the saw, followed by further shredding and grinding with a knife and grinder (Panasonic miller) respectively to give samples size of approximately 0.2-0.5 cm.

3.2. Subcritical Water Extraction

Batch (static) laboratory-size subcritical water extractor with the heating bath system (Model Celsius 600H, Thomas Kagaku, Japan,) was used in this study. There are two distinct heating baths which is oil and salt bath. The oil bath, which employs silicon oil for heating the reactor (containing the mixture of sample and water) during the extraction, was used for temperatures ranging from 100 to 170 °C. The salt bath (mixture of potassium nitrate salt and sodium nitrate salt) meanwhile was used for temperatures ranging from 180 to 271 °C. Both the heating baths an agitator/mixer to distribute the heat uniformly during the extraction process. Batch laboratory-size SWE also 1640 mm length stainless steel reactors (SUS316) with inner reactor cap diameter of 75/164 mm and outer reactor cap diameter of 180/270 mm) (Fig. 1). The inner volume of the reactor 8.0×10^{-6} m^3 and the system can be operated until maximum operating pressure of 22 MPa (around 374 °C).

For each extraction, a mixture of grinded, dried raw-sample and distilled water was added to the reactor and argon gas was used to remove the oxygen and air from the mixture and reactor. Then, the cap was placed on the reactor, and the reactor was sealed completely. When the 20 L heating bath (oil/salt) attained the required temperature within 10 to 15 minutes, the reactor was immersed for a
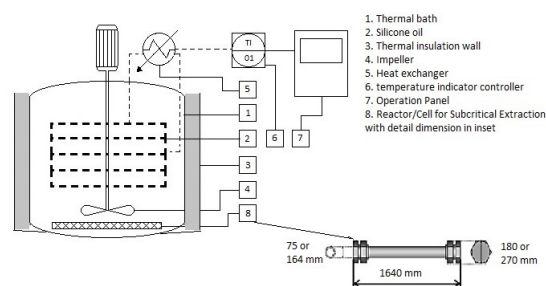

Fig. 1. Schematic diagram of SWE system with its components

specified time (1-34 min according to design of experiments [25]). Once the reaction was completed, the reactor was taken out and cooled down with water for 1 to 2 hours.

Next, the essential oil in the aqueous mixture (contained water and essential oil) was recovered using liquid-liquid extraction. In this step, the liquid mixture was transferred into a separation funnel and hexane was added to remove the essential oil from the mixture. Finally, the hexane was eliminated using rotary evaporator (Buchi). Finally, sodium sulfate anhydrous was utilized to remove any moisture or water from the essential oil (Fig. 2). The extracted essential oils were stored in dark-sealed-vial at 4 °C for further analysis. The yield of essential oil extracted was calculated using the volume of collected essential oil (mL) divided by weight of the plant material (g) [7]. The formula is as given below:

$$y = \frac{V \times 100}{W} \tag{14}$$

where y is the yield of essential oil (% v/w), V is the volume of collected essential oil (mL) and W is the weight of the plant material (g). The volume of the oil was measured using small graduated cylindrical and weight of plant material was measured using weighing scale.
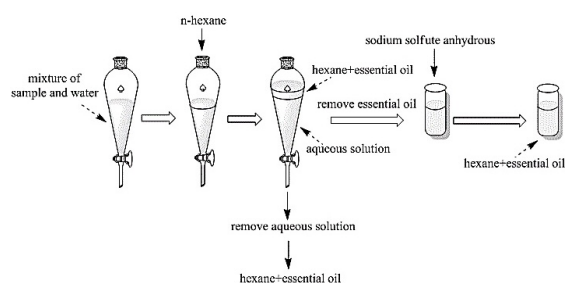

Fig. 2. Liquid-liquid extraction process of essential oil

3.3. Mechanism and Kinetic Study

The mechanism and kinetics of *A. malaccensis'* wood oil extraction via subcritical water were studied at different temperatures of 115 °C, 182 °C and 250 °C based on the values randomly suggested by Design Expert 7 software [25]. These data were later assessed by fitting to all four models as mentioned previously. The mass transfer and kinetic models were solved using the non-linear least square fitting (NLSF) approach, facilitated by Microsoft Excel's SOLVER function as an interface and operated based on the iterative algorithm that minimized the sum of squared residual or error between the data points. Consequently, the quality of the models' fit was assessed by evaluating the sum of squared residuals (SSR) (Eq. (15)) and the coefficient of determination (R^2) through the correlations presented in Eqs. (16) to (18). SSR nearing zero and (R^2) nearing unity indicate the model agreement to the observations data.

$$SSR = \sum \left(y_{(t)} - \hat{y}_{(t)} \right)^2 \tag{15}$$

$$R^2 = 1 - \frac{SSR}{SST} \tag{16}$$

SST is the total sum of squares obtained by the following equation,

$$SST = \sum \left(y_{(t)} - \bar{y}_{(t)} \right)^2 \tag{17}$$

Hence, alternatively expressed as,

$$R^2 = 1 - \frac{\sum \left(y_{(t)} - \hat{y}_{(t)} \right)^2}{\sum \left(y_{(t)} - \bar{y}_{(t)} \right)^2} \tag{18}$$

where $y_{(t)}$ is the observed or experimental value of the data. $\hat{y}_{(t)}$ is the estimated value of the data. $\bar{y}_{(t)}$ is the mean value of the data.

Finally, by knowing the rate constants, k of the extraction at different temperatures, the activation energy (E_a) can subsequently be obtained through linearization of Arrhenius equation.

4. Result and discussions

4.1. Reaction mechanism and kinetics modelling

Based on previous optimization studies by Samadi et al. [36], the temperature was considered as the most significant parameter affecting the EO yield extracted through the SWE method from *Aquilaria Malaccensis* wood. Thus, a time-dependent experiment was performed to observe the effect of temperature on the EO yield with time. The EO yield extracted was plotted as a function of time for a varied extraction temperature (115 °C, 182 °C, and 250 °C) as suggested by optimization work conducted previously [25].

As indicated in Fig. 3, all graphs at different temperatures exhibited an analogous trend, where the EO yield increases progressively with an increasing extraction time, up to 25 minutes, then gradually increases till 30 minutes before remaining plateau or slightly decreased as the time extended. A higher temperature could significantly affect the sample matrix and solvent characteristics and increase yield [36]. Our findings here confirmed this expectation where the EO yield was the highest at 250 °C compared to 182 °C and 115 °C, due to the enhanced sample dissolution and solvent solubility.
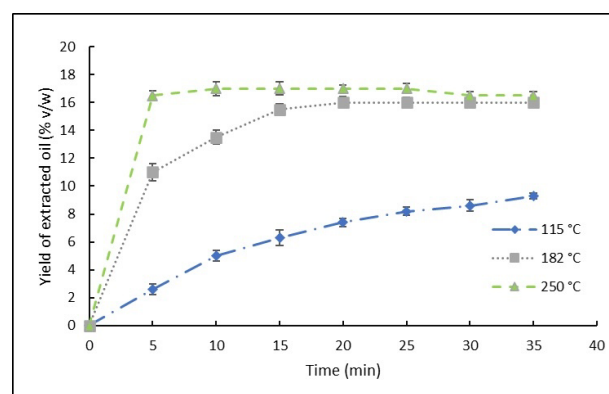

Fig. 3. Essential oil of *A. malaccensis* wood concentration profile with time using subcritical extraction at the 115 °C, 182 °C and 250 °C

This outcome can be elucidated by the decrease in water's dielectric constant and polarity as temperature rises, which enhances water's effectiveness for extracting essential oils from wood at elevated temperatures, akin to organic solvents, as observed in previous studies [16, 30, 34, 35]. Additionally, the increased rate and yield of essential oil at higher temperatures may be ascribed to the greater availability of energy, which makes it easier to break plant cell walls under these conditions. It is also important to note that wood samples were used in this work. Unlike other plant part such as leaves that has simpler structure comprising of cell wall with cellulose, non-cellulosic, polysaccharides, proteins, phenolic compounds, and others, wood samples however have more complex structure comprising of long polymer of cellulose, hemicellulose impregnated with membrane complex structure. The nature of wood hence provides greater barrier to the extraction of essential oil compared to other parts of plants.

With the extension of the extraction duration, the extracted essential oil (EO) yields at all three temperatures began to diminish, indicating the initiation of degradation in the lower molecular EO compounds. This gradual decline in EO yield becomes more noticeable over time,

particularly at 250 °C and 182 °C, in contrast to 115 °C. This suggests that elevated temperatures exceeding 150°C can significantly accelerate the deterioration of EO during prolonged extraction.

As mentioned earlier, the controlling mechanism of SWE may differ in various instruments, samples, and conditions, thus kinetic studies were performed by fitting the experimental data to four different models involving one-site kinetic desorption model, second-order rate law model, two-site kinetic desorption model, and partitioning coefficient with external mass transfer model. Here, SSR and R2 were selected as the values for best fitting criteria.

The result in Table 1 and Fig. 4 showed that the first order model has a low average of R^2 (<0.81) with k values decreasing with increment of temperature. These results is certainly not in coherent with results in Fig. 3, which shows that the yield concentration profile with time increases with time and proceeded in two significant behaviours of fast extraction and slow extraction. An increment of yield with temperature as shown in Fig. 3 would mean an increase in the value of rate constants, *k*. Furthermore, the first order model being a linear relationship having only one kinetic rate constant, assumes that the extraction process happens through one simultaneous process [32, 35, 40]. This obviously could not describe the behaviour of the SWE of essential oil from *Aquilaria Malaccensis* wood at all different extraction temperatures as seen in Fig. 3. The decrease of rate constant, k with time also contradicts with findings from Samadi et al. [36] which stated that the yield of essential oil increases with increasing temperature. Hence, the first order model was unable to properly explain the extraction of the *A. malaccensis* wood essential oil by subcritical water extraction.

Table 1. Kinetic and fitting parameters of one-site kinetic desorption model for SWE wood

Extraction Temperature	One-site kinetic desorption model	
	$k(min^{-1})$	R^2
115 °C	0.03	0.43
182 °C	0.0105	0.65
250 °C	0.0004	0.81
Average		**0.63**

In contrast to first-order model, the second-order model showed very good fit (R^2>0.98) and low SSR value (<0.02) with the experimental data and strongly suggested that the subcritical water extraction of *A. malaccensis* wood oil followed a second order model (Fig. 5 and Table 2). In contrast to the first-order model, second-order model assumes that the extraction happens in two simultaneous processes.
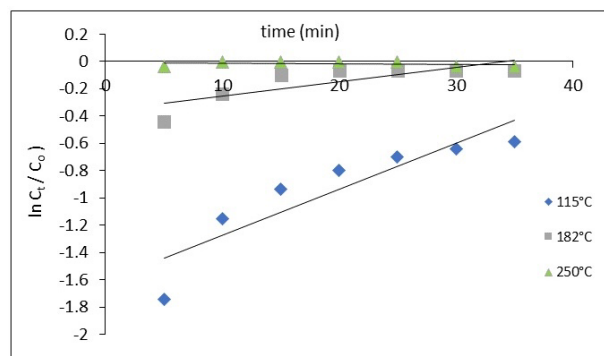

Fig. 4. *A. malaccensis* wood essential oil yield plot for estimating the k1 values for first order kinetic model $\left(\frac{C_t}{C_\infty} = 1 - e^{k_1 t} \right)$ at SWE temperature

Hence, this assumption might be the reason for the better fit between this model and experiment results. *k* values which reflect the rate of desorption of essential oil from the sample particles [35], were determined by linearization (Fig. 6) and was found to be significantly increased from 0.03 to 2.5 (Table 2) for temperature 115 °C and 250 °C respectively. In other words, the increase of extraction temperature, increased the desorption rate of *A. malaccensis* wood essential oil (*k* value). Higher desorption rate (*k*) and better extraction at higher temperatures may be explained by the fact that both the surface tension of water (i.e. solvent) and its viscosity tend to reduce with the rise in extraction temperature [35]. So, the increase of temperature resulted in increase in rate of the extraction due to better performance of water (low polarity and dielectric constant) [16, 30, 35]. Furthermore, the increase in the rate of extraction may be explained by the availability of higher energy in higher temperatures that facilitates the breakage of cell-walls and consequently result in faster extraction.

Table 2. Kinetic and fitting parameters of second-order rate law model for SWE of wood

Extraction Temperature	Second-order rate law model		
	$k(min^{-1})$	SSR	R^2
115 °C	0.03	0.02877	0.989
182 °C	0.4	0.00512	0.993
250 °C	**2.5**	0.00584	0.994
Average		**0.01324**	**0.992**

The analysis of kinetics was continued with the two-site kinetic model that assumes that extraction occurs in two stages (fast and slow desorption). It assumes that the essential oil near the surface or inside damaged cells is quickly extracted (fast desorption, k_1), while the solute residing
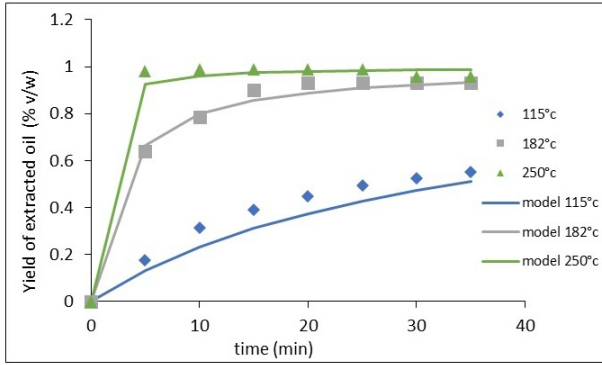
Fig. 5. Second order kinetic model of extraction of *A. malaccensis* wood oil by SWE at various temperatures
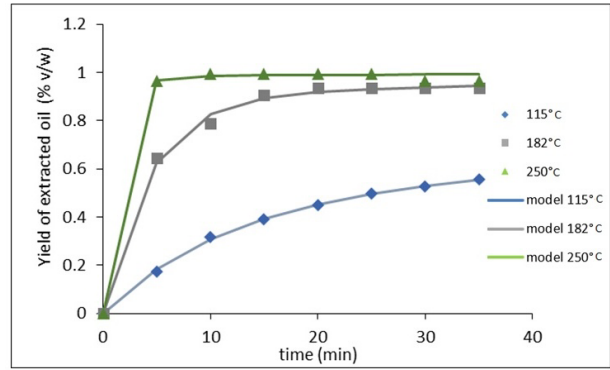

Fig. 7. Two-site desorption kinetic model of extraction of *A. malaccensis* wood oil by SWE at various temperatures
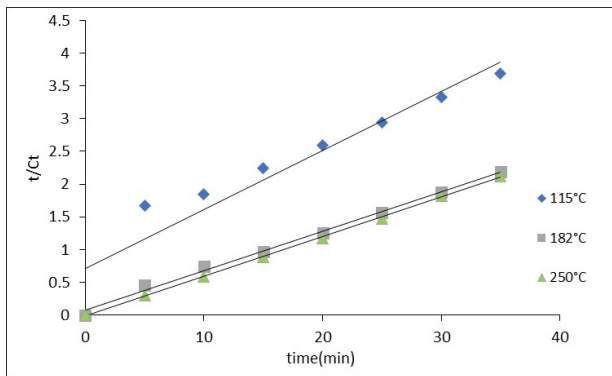

Fig. 6. *A. malaccensis* wood essential oil yield plot for estimating the k_2 value for second order kinetic model $\left(\frac{t}{c_t} = \frac{1}{k_2 c_\infty^2} + \frac{1}{c_\infty} t \right)$ at SWE temperature

inside the interior of intact cells, slowly diffuses to the surface of plant material (slow desorption, k_2) simultaneously [28]. In contrary to the first and second-order models, two-site kinetic model consists of two kinetic-rate constants for describing fast and slow desorption of the essential oil.

From Fig. 7, most of the yield was extracted during the first 10 minutes of the extraction process (fast desorption) at extraction temperatures of 182 and 250 °C and the rest of the essential oil was extracted later after 10 minutes (slow desorption). Hence, both the fast and slow desorption phases of the essential oil from wood particles are very apparent Fig. 7.

The results in Table 3 showed that both fast (k_1) and slow (k_2) kinetic rate constant (determined by using Microsoft EXCEL solver by minimizing the errors) increased with the rise in extraction temperature. This finding also indicates that the increase of temperature resulted in faster and easier desorption of volatile compounds from the *A. malaccensis* wood particles. The improvement of the extraction at higher temperatures can be explained again by

the fact that both water viscosity and dielectric constant have a tendency to go down when temperature rises [35]. The findings indicated that there is a good fit between the experiment and two-site kinetic model at all temperatures (Table 3 and Fig. 7) with R^2 greater than 0.99 and SSR less than 0.002.

In addition, the R^2 and SSR values of two-site desorption model were also slightly higher and lower respectively in comparison to that of second order model indicating better fitting with experimental data at all temperature compared to second order model. In short, the two-site desorption model was able to better describe the subcritical water extraction of essential oil from *Aquilaria Malaccensis*.

Partitioning coefficient with external mass transfer model includes two constants of k_D (partitioning equilibrium) and $k_e a_p$ (overall volumetric mass transfer coefficient). Based in Eq. (11), faster extraction rate favours lower k_D and high $k_e a_p$. Fig. 7 shows the analysis of the experimental data with the external mass transfer/partitioning model which presented a good fitting based on kD (partitioning equilibrium) and keap (overall volumetric mass transfer coefficient) values. The rise in extraction temperature leads to an increase of keap as expected due to the increment in the diffusivity (Fickian diffusion) and external mass transfer (i.e. rapid hydroscopicity of the extraction matrix) and shortens the time of extraction [30, 35].

On the other hand, k_D values decreased with the increase of the extraction temperature as predicted to yield faster extraction rate at higher temperatures. k_D is a partitioning equilibrium factor and defined as the solute concentration in the matrix to that in the extraction fluid. The decrease in k_D values is because of the increased solubility of solute in water as temperature rise since at subcritical conditions, water-polarity turned lower and pressure within the plant-cells became higher. This thus expedites

Table 3. Kinetic and fitting parameters of two-site kinetic desorption model for SWE of wood

Extraction Temperature	F	Two-site kinetic desorption model			
		$k_1(min^{-1})$	$k_2(min^{-1})$	SSR	R^2
115 °C	0.51	0.0055	0.0847	0.00015	0.999
182 °C	0.1009	0.0169	0.232	0.00236	0.997
250 °C	0.0155	0.02	0.788	0.00136	0.998
Average				**0.00129**	**0.998**

the extraction of essential oil at high temperatures [32].

The result of thermodynamic partition with external mass transfer resistance model was consistent with other studies [32, 35, 40], who also reported the increase of $k_e a_p$ and decrease of k_D with the temperature. The findings showed a good fit between the experiments data and the proposed model at almost all temperatures (Fig. 8) with R^2 around 0.94, 0.97 and 0.99 for 115 °C, 182 °C and 250 °C respectively. SSR values meanwhile range from 0.002 to 5.1 for the studied temperature. However, compared to the two-site kinetic model, the portioning/external mass transfer R^2 values were lower and SSR values were bigger.
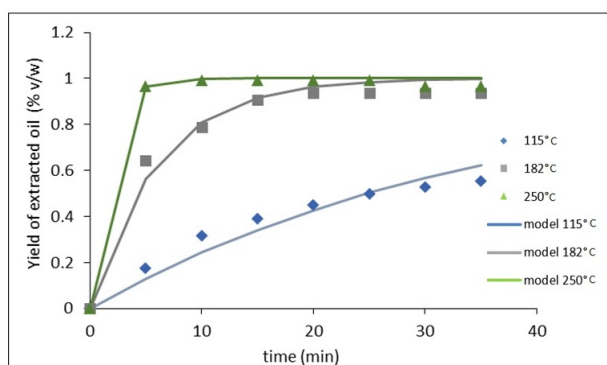

Fig. 8. Partitioning coefficient with external mass transfer kinetic model of extraction of *A. malaccensis* wood oil by SWE at various temperatures

In order to find the kinetic model that best elucidates the subcritical water extraction of essential oil from wood of *A. malaccensis*, all the above-mentioned kinetic models were compared with each other quantitatively based on coefficient of determination, R^2 and SSR values. The results indicated that "two-site kinetic", "second order", and "partitioning coefficient with mass transfer" models were suitable for explaining the extraction of wood essential oil by subcritical water extraction. Both the second order and two-site kinetic model desirably explained the subcritical extraction of *A. malaccensis* wood essential oil across all the temperatures kinetically, while partitioning coefficient with mass transfer model described the extraction mechanism

thermodynamically.

Although all three models were able to explain the extraction mechanism, the two-site kinetic model demonstrated the highest coefficient of determination (R^2) and lowest SSR at all studied temperature compared to other kinetic models (Tables 2 to 4). Thereby, despite the acceptable fit between all the models and experiment data, the two-site kinetic model was concluded to be the best kinetic model for explaining the extraction of essential oil from *A. malaccensis* wood using SWE at all temperatures. This result was in agreement with other kinetic studies on subcritical water extraction work. Those investigations include the work done by Islam et al. [35] on the SWE of PAHs from soil, Duba et al. [34] on the SWE of polyphenols from grape skin/seed and Kim and Lim [33] on the extraction of flavonoids from *citrus inshiu* peels.

4.2. Determination of activation energy (E_a)

Once the rate-constants of the extraction at different temperatures were obtained for the two-site kinetic models (the best fitted), the activation energy (E_a) was calculated using the Arrhenius equation. The activation energy (E_a) reflects the amounts of energy required for a reaction to occur [32] and the results are as in Fig. 9. For each stage of the process, the Arrhenius plot appeared to be linear where the logarithm of k decreased linearly with increasing 1/T. Through best fitting by linearization, the interception and slope were obtained and the activation energies were calculated. E_a values for fast and slow desorption steps in the extraction of essential oil from *A. Malaccensis* wood using SWE was found to be 16.6 and 28 KJ/mol respectively with R^2 of 0.90 and 0.98. The amount of activation energy was found to be consistent with other studies using SWE [33, 34]. The values of E_a found here are consistent with the k values found from the two-site kinetic model. k_2 having higher corresponds to higher Ea and vice versa for lower k_1 values.

Table 5 shows that low activation energy value was obtained at the fast desorption (k_1) where the essential oil near the surface or inside damaged cells is quickly extracted while high E_a was calculated for the slow diffusion (k_2)

Table 4. Kinetic and fitting parameters of Partitioning coefficient with external mass transfer model for SWE of wood

Extraction Temperature	Partitioning coefficient with external mass transfer			
	k_D	$k_e a_p (min^{-1})$	SSR	R^2
115 °C	1.883	0.0525	0.01655	0.941
182 °C	0.525	0.306	5.16606	0.979
250 °C	0.472	0.315	0.00259	0.997
Average			**1.7284**	**0.9723**
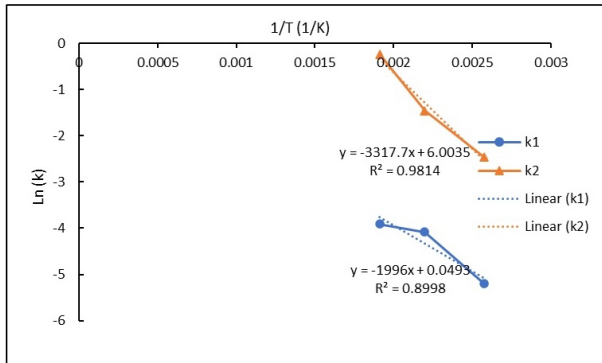
Fig. 9. The plot ln k versus 1/T for SWE

of the solute residing inside the interior of intact cells to the surface of plant. Our findings are similar to Dao et al. [44] whose work also fitted two-site kinetic model. They reported a low activation energy value for unhindered diffusion (96 kJ/mol) and high activation values (167 kJ/mol) for washing steps in the extraction of essential oil from pomelo by simultaneous washing and unhindered model. Their experimental data also agreed well with two-site kinetic model. These can be attributed to the characteristics of an extraction process of a physical nature. In our work, it was also found that the frequency value, *A* of the fast phase was approximately 380 times greater than that of the diffusion phase (Table 5) which maybe due to the nature of samples that was used in this work.

Table 5. Parameters of Arrhenius Equation

Parameters	Fast desorption	Slow Desorption
E_a (kJ/mol)	16.6	28
A (min^{-1})	1.05	404
R^2	0.9	0.98

5. Conclusion

A. malaccensis' oil was extracted by subcritical method from its wood and the behaviour was kinetically modelled. The temperature is the most important parameter since dra-

matic changes in oil yield were observed with higher temperatures improved extraction efficiency. The experimental extraction profiles obtained at 115 °C, 182 °C and 250 °C were described to one and two-site kinetic desorption models, second order model and partitioning coefficient with mass transfer model. Based on high R^2 and low SSR, the two-site kinetic model appeared to be the best model to describe the Subcritical Water Extraction (SWE) mechanisms which happened in two stages of fast and slow desorption. Two values of rate constants for fast, k_1 and slow desorption, k_2 in the two-site kinetics model were calculated and a higher k_2 value than k_1 was found. Further analysis of the activation energy, E_a recorded a lower value for easy, fast desorption compared to slow desorption. All these results conformed well to the nature of fast desorption for the movement of the essential oil residing in the cells with broken walls or near to the surface and slow desorption for diffusion of the solute at the interior of intact cells. Conclusively, the model analysis has given greater insights on the controlling steps of essential oil extraction in SWE process, its optimization and practical scaling up approach.

6. Acknowledgements

References

[1] A. Asbahani, M. El, K. Badri, W. Sala, M. Addi, and E. H. A. Casabianca, (2015) *"Essential oils: From extraction to encapsulation"* **International Journal of Pharmaceutics** *483*(1-2): 220–243. DOI: 10.1016/j.ijpharm.2014.12.069.

[2] J. S. Raut and S. M. Karuppayil, (2014) *"A status review on the medicinal properties of essential oils"* **Industrial Crops and Products** *62*: 250–264. DOI: 10.1016/j.indcrop.2014.05.055.

[3] C. B. K. Hüsnü and F. Demirci. "Chemistry of Essential Oils". In: *Flavours and Fragrances: Chemistry, Bioprocessing and Sustainability*. Ed. by R. G. (Berger. Berlin, Heidelberg: Springer, Berlin, Heidelberg, 2007, 43–86. DOI: 10.1007/978-3-540-49339-6_4.

[4] A. Barden, N. A. Anak, T. Mulliken, and M. Song. *Heart of the Matter: Agarwood Use and Trade and CITES Implementation for Aquilaria malaccensis*. Cambridge: TRAFFIC International, 2000.

[5] W. Dhifi, S. Bellili, S. Jazi, N. Bahloul, and W. Mnif, (2016) *"Essential Oils' Chemical Characterization and Investigation of Some Biological Activities: A Critical Review"* **Medicines (Basel). 3**(4): 25. DOI: 10.3390/medicines3040025.

[6] J. Sharifi-Rad, A. Sureda, G. C. Tenore, M. Daglia, M. Sharifi-Rad, M. Valussi, R. Tundis, M. Sharifi-Rad, M. R. Loizzo, A. O. Ademiluyi, and R. Sharifi-Rad, (2017) *"Biological Activities of Essential Oils: From Plant Chemoecology to Traditional Healing Systems"* **Molecules 22**(1): 70. DOI: 10.3390/molecules22010070.

[7] M. A. Desai, J. Parikh, and A. K. De, (2014) *"Modelling and optimization studies on extraction oflemongrass oil from Cymbopogon flexuosus (Steud.) Wats"* **Chemical Engineering Research and Design 9**(5): 793–803. DOI: 10.1016/j.cherd.2013.08.011.

[8] N. Yoswathana, M. N. Eshiaghi, and K. Jaturapornpanich, (2012) *"Enhancement of Essential Oil from Agarwood by Subcritical Water Extraction and A Pretreatments on Hydrodistillation"* **International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering 6**(5): 453–459. DOI: 10.5281/zenodo.1060381.

[9] N. Sulaiman, M. I. Idayu, A. Z. Ramlan, M. N. Fashya, A. N. N. Farahiyah, J. Mailina, and M. A. N. Azah, (2015) *"Effects of extraction methods on yield and chemical compounds of gaharu (aquilaria malaccensis)"* **Journal of Tropical Forest Science 27**(3): 413–419.

[10] K. N. Fazila and K. K. Halim, (2012) *"Effects of soaking on Yield and Quality of Agarwood Oil"* **Journal of Tropical Forest Science 24**(4): 557–564.

[11] S. N. Tajuddin and M. M. Yusoff, (2010) *"Chemical Composition of Volatile Oils of Aquilaria malaccensis (Thymelaeaceae) from Malaysia"* **Natural Product Communications 5**(12): 1965–1968. DOI: 10.1177/1934578X1000501229.

[12] C. U. Tam, F. Q. Yang, Q. W. Zhang, J. Guan, and S. P. Li, (2007) *"Optimization and comparison of three methods for extraction of volatile compounds from Cyperus rotundus evaluated by gas chromatography-mass spectrometry"* **Journal of Pharmaceutical and Biomedical Analysis 44**(2): 444–449. DOI: 10.1016/j.jpba.2006.10.026.

[13] W. Abdelmoez, E. Ashour, S. M. Naguib, A. Hilal, D. A. A. Mahdy, E. A. Mahrous, and E. Abdel-Sattar, (2016) *"Kinetic and thermodynamics studies for castor oil extraction using subcritical water technology"* **Journal of Oleo Science 65**(6): 477–485. DOI: 10.5650/jos.ess15298.

[14] R. S. Ayala and M. D. L. de Castro, (2001) *"Continuous subcritical water extraction as a useful tool for isolation of edible essential oils"* **Food Chemistry 75**(1): 109–113. DOI: 10.1016/S0308-8146(01)00212-6.

[15] I. Okajima and T. Sako, (2014) *"Energy conversion of biomass with supercritical and subcritical water using large-scale plants"* **Journal of Bioscience and Bioengineering 117**(1): 1–9. DOI: 10.1016/j.jbiosc.2013.06.010.

[16] C. C. Teo, S. N. Tan, J. W. H. Yong, C. S. Hew, and E. S. Ong, (2010) *"Pressurized hot water extraction (PHWE)"* **Journal of Chromatography A. 1217**(16): 2484–2494. DOI: 10.1016/j.chroma.2009.12.050.

[17] D. Li, Z. Zhang, S. Liu, and S. Li., (2020) *"Understanding nano-modification in liquid dielectric from coefficient of viscosity"* **AIP Advances 10**(8): 085009. DOI: 10.1063/5.0015090.

[18] P. W. Carr, D. R. Stoll, and X. Wang, (2011) *"Perspectives on recent advances in the speed of high-performance liquid chromatography"* **Analytical Chemistry 83**(6): 1890–1900. DOI: 10.1021/ac102570t.

[19] M. Plaza and C. Turner, (2015) *"Pressurized hot water extraction of bioactives"* **TrAC Trends in Analytical Chemistry 71**: 39–54. DOI: 10.1016/j.trac.2015.02.022.

[20] M. Plaza and M. L. Marina, (2019) *"Pressurized hot water extraction of bioactives"* **TrAC Trends in Analytical Chemistry 116**: 236–247. DOI: 10.1016/j.trac.2019.03.024.

[21] Y. Wang, Y. Ye, L. Wang, W. Yin, and J. Liang, (2021) *"Antioxidant activity and subcritical water extraction of anthocyanin from raspberry process optimization by response surface methodology"* **Food Bioscience 44**: 10139. DOI: 10.1016/j.fbio.2021.101394.

[22] M. E. Yulianto, B. Jos, and B. Budiyono, (2023) *"Kinetic modelling of liquid-solid extraction of bioactive compounds from ginger waster using subcritical water"* **Sainteknol: Jurnal Sains dan Teknologi** *21*(1): 28–35. DOI: 10.15294/sainteknol.v21i1.44589.

[23] N. Sabil, S. A. Toat, Y. Hiroyuki, and S. Izhar, (2023) *"Hydrolysis of blended cotton/polyester fabric from hospital waste using subcritical water"* **Sains Malaysiana** *52*(1): 139–151. DOI: 10.17576/jsm-2023-5201-11.

[24] N. A. A. Halim, Z. Z. Abidin, S. I. Siajam, C. G. Hean, and M. R. Harun, (2021) *"Optimization studies and compositional analysis of subcritical water extraction of essential oil from citrus hystrix DC. Leaves"* **The Journal of Supercitical Fluids** *178*(10538): 1–16. DOI: 10.1016/j.supflu.2021.105384.

[25] M. Samadi, Z. Z. Abidin, H. Yoshida, R. Yunus, R., and D. R. A. Biak, (2020) *"Towards Higher Oil Yield and Quality of Essential Oil Extracted from Aquilaria malaccensis Wood via the Subcritical Technique"* **Molecules** *25*(17): 3872. DOI: 10.3390/molecules25173872.

[26] M. A. Bezerra, R. E. Santelli, E. P. Oliveira, L. S. Villara, and L. A. Escaleira, (2008) *"Response surface methodology (RSM) as a tool for optimization in analytical chemistry"* **Talanta** *76*(5): 965–977. DOI: 10.1016/j.talanta.2008.05.019.

[27] F. Reyes-Jurado, A. Franco-Vega, and N. Ramírez-Corona, (2014) *"Essential Oils: Antimicrobial Activities, Extraction Methods, and Their Modeling"* **Food Engineering Review** *7*: 275–297. DOI: 10.1007/s12393-014-9099-2.

[28] A. H. Asl and M. Khajenoori. "Chapter 4: Modelling of Subcritical Water Extraction". In: *Green Extraction in Separation Technology*. Boca Raton: CRC Press, 2021, 85–113.

[29] C. Chan, R. Yusoff, and G. Ngoh, (2014) *"Modeling and kinetics study of conventional and assisted batch solvent extraction"* **Chemical Engineering Research and Design** *92*(6): 1169–1186. DOI: 10.1016/j.cherd.2013.10.001.

[30] Y. Ho, H. A. Harouna-oumarou, H. Fauduet, and C. Porte, (2005) *"Kinetics and model building of leaching of water-soluble compounds of Tilia sapwood"* **Separation and Purification Technology** *45*(3): 169–173. DOI: 10.1016/j.seppur.2005.03.007.

[31] H. S. Kusuma and M. Mahfud, (2018) *"Kinetic studies on extraction of essential oil from sandalwood (Santalum album) by microwave air-hydrodistillation method"* **Alexandria Engineering Journal** *57*(2): 1163–1172. DOI: 10.1016/j.aej.2017.02.007.

[32] M. Khajenoori, A. H. Asl, and F. Hormozi, (2009) *"Proposed Models for Subcritical Water Extraction of Essential Oils"* **Chinese Journal of Chemical Engineering** *17*(3): 359–365. DOI: 10.1016/S1004-9541(08)60217-7.

[33] D. S. Kim and S. B. Lim, (2020) *"Kinetic study of subcritical water extraction of flavonoids from citrus unshiu peel"* **Separation and Purification Technology** *250*: 117259. DOI: 10.1016/j.seppur.2020.117259.

[34] K. S. Duba, A. A. Casazza, H. B. Mohamed, P. Perego, and L. Fiori, (2015) *"Extraction of polyphenols from grape skins and defatted grape seeds using subcritical water: Experiments and modeling"* **Food Bioproduct Process** *94*: 29–38. DOI: 10.1016/j.fbp.2015.01.001.

[35] M. N. Islam, Y. T. Jo, S. K. Jung, and J. H. Park, (2013) *"Thermodynamic and kinetic study for subcritical water extraction of PAHs"* **Journal of Industrial Engineering and Chemistry** *19*(1): 129–36. DOI: 10.1016/j.jiec.2012.07.014.

[36] M. Samadi, Z. Z. Abidin, H. Yoshida, R. Yunus, D. R. A. Biak, C. H. Lee, and E. H. Lok, (2019) *"Subcritical water extraction of essential oil from Aquilaria malaccensis leaves"* **Separation Science and Technology** *55*(5): 1–20. DOI: 10.1080/01496395.2019.1650768.

[37] D. D. Paunovic, S. S. Mitic, D. A. Kostic, M. N. Mitic, B. T. Stojanovic, and J. L. Pavlovic, (2014) *"Kinetics and thermodynamics of the solid-liquid extraction process of total polyphenols from barley"* **Advanced technologies** *3*(2): 58–63. DOI: 10.5937/savteh1402058P.

[38] N. Rahimi, M. Shiva, S. A. Mortazavi, A. H. Elhamirad, A. M. Maskooki, and G. Rajabzadeh, (2015) *"Kinetic study of superheated water extraction of berberine from Berberis vulgaris root"* **Bulgarian Chemical Communications** *47*(D): 140–146.

[39] H. M. Hazwan, C. M. Hasfalina, J. Hishamuddin, and Z. A. Zurina, (2012) *"Optimization and Kinetics of Essential Oil Extraction from Citronella Grass by Ohmic Heated Hydro Distillation"* **International Journal of Chemical Engineering and Applications** *3*: 173–177. DOI: 10.7763/IJCEA.2012.V3.181.

[40] T. Anekpankul, M. Goto, M. Sasaki, P. Pavasant, and A. Shotipruk, (2007) *"Extraction of anti-cancer damnacanthal from roots of Morinda citrifolia by subcritical water"* **Separation and Purification Technology** *55*(3): 343–349. DOI: 10.1016/j.seppur.2007.01.004.

[41] Y. Ho and G. McKay, (1999) *"Pseudo-second order model for sorption processes"* **Process Biochemistry** *34*(5): 451–465. DOI: 10.1016/S0032-9592(98)00112-5.

[42] D. Cox-Georgia, N. Ramadoss, C. Dona, and C. Basu, (2019) *"Therapeutic and Medicinal Uses of Terpenes"* **Medicinal Plants**: 333–59. DOI: 10.1007/978-3-030-31269-5_15.

[43] D. L. Sidebottom, (2012) *"Introduction to phase transitions"* **Fundamentals of Condensed Matter and Crystalline Physics: An Introduction for Students of Physics and Materials Science** *66*(5): 267–288. DOI: 10.1063/PT.3.1980.

[44] T. P. Dao, T. V. N. Y. N. Tran, X. T. Le, T. N. T. An, N. H. T. Anh, and L. G. Bach, (2021) *"Central Composite Design, Kinetic Model, Thermodynamics, and Chemical Composition of Pomelo (Citrus Maxima (Burm.) Merr.) Essential Oil Extraction by Steam Distillation"* **Processes** *9*(11): 2075. DOI: doi.org/10.3390/pr9112075.

[45] A. Ramanathan and V. Thangarasu, (2019) *"Effect of high-frequency microwave irradiation on Aegle Marmelos Correa oil extraction: Kinetic and thermodynamic study"* **Energy Procedia** *158*: 1046–1051. DOI: 10.1016/j.egypro.2019.01.253.

[46] S. B. D. Santos, M. A. Martins, A. L. Caneschi, P. R. M. Aguilar, and J. S. D. R. Coimbra, (2015) *"Kinetics and Thermodynamics of Oil Extraction from Jatropha curcas L. Using Ethanol as a Solvent"* **International Journal of Chemical Engineering** *2015*: DOI: 10.1155/2015/871236.

[47] O. S. Stamenkovic, M. D. Kostic, M. B. Tasic, I. G. Djalovic, P. M. Mitrovic, M. O. Biberdžić, and V. B. Veljkovic, (2020) *"Kinetic, thermodynamic and optimization study of the corn germ oil extraction process"* **Food and Bioproducts Processing** *120*: 91–103. DOI: 10.1016/j.fbp.2019.12.013.