Experimental and Kinetic Modeling Studies on Extraction of Essential Oil from Vietnamese Calamondin (*Citrus microcarpa*) by Hydro-Distillation Process

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ABSTRACT: *Current research refers to the modeling of data from the extraction of essential oils from plant materials via the hydro-distillation method, which is applicable from the laboratory scale to the production scale. Experimental data from the process were obtained by studying the kinetics of the distillation of calamondin peel essential oil. Kinetic models are based on the extraction mechanism of the essential oil, which involves the amount of essential oil released from the plant cell. On the principle of extracting essential oils, the mechanism of washing and diffusing is the basis for constructing the kinetic model and its assumption is developed in order to give an appropriate model. The descriptive kinetics of the hydro-distillation process are based on two assumptions: instantaneous washing followed by non-stationary diffusion and first-order kinetics (diffusion without washing). These two models were compared to select the optimal model for the extraction process. The results showed that the calamondin peel essential oil extraction process was described by a non-stationary model with an extraction rate constant (k) of 0.038 min^{-1}. The extraction of hydro-distillation essential oil from calamondin peels obtained the highest essential oil content (4.2%) under extraction conditions such as a water-material ratio of 3:1 mL/g, a heating power of 204 W, and an extraction time 60 min. Furthermore, the chemical composition of volatiles present in calamondin peel oil was evaluated for the sample by using GC-MS. Limonene (88.637%), Germacrene D (4.451%), and β-Edudesmol (1.034%) were the major constituents in the essential oils.*

KEYWORDS: *Citrus microcarpa; Essential oil; Kinetics modeling; Hydro-distillation; GC-MS.*

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INTRODUCTION

In recent years, the preference for natural products has been increasing, causing the market for products to expand significantly. Natural products [1-6] today are noted for their functional properties such as antibacterial, antifungal, anti-parasitical activities, which are widely applied in cosmetics or pharmaceuticals industries. Especially, aromatic compounds from plants such as essential oils are of particular interest. Essential Oil (EO, also known as volatile) is a liquid, a mixture of volatile constituents, characterized by a strong aroma and primarily produced from plant materials (flowers, leaves, bark, seeds, stems, and roots [7-11]) as secondary metabolites. Essential oils are very complex natural mixtures of lipophilic substances, comprising of 20-60 different components [12]. However, essential oils are characterized by two or three major components such as limonene, carvacrol, and citral, in high content (20-90%) compared to other components at trace level. These major components are used to determine its properties as well as the quality of essential oil.

Citrus peels such as orange, lemon, mandarin, pomelo, and calamondin have been long-term used to produce essential oils in many industrialized countries around the world. Citrus essential oils possess a pleasant aroma and a high content of Limonene (≥ 90%) which is widely used in many fields of cosmetics, pharmaceuticals, and food [13]. Recent scientific results have reported that Limonene has shown potential in anti-pancreatic cancer and anti-breast cancer [14].

In Vietnam, especially in the Mekong Delta, the calamondin (*Citrus microcarpa* Lour), a member of the *Rutaceae* family, is widely cultivated in tropical/subtropical regions such as the Philippines, Japan, China, and Vietnam [12, 15]. Calamondin fruit has a small shape, an average diameter of 25-35 mm, and a thin peel. Calamondin is harvested all year round, the samples for the extraction can be prepared from dried, fresh, or frozen peels before conducting the extraction process. The availability of raw materials generates great advantages in the study or production-scale of Citrus essential oils.

To obtain essential oils, there are various methods of extraction such as hydro-distillation, microwave-assisted extraction, solvent extraction, supercritical fluid extraction, and steam distillation [16-21]. Hydro-distillation method has increasingly become popular for extracting essential oils from plants with the simplicity in equipment as well as system installation and relatively high recovery efficiency [22]. In this study, vapors of the essential oils mixture and water during heating are liquified in the condenser. The extraction of hydro-distillation plays an important role in preserving the biological activities in essential oils such as antibacterial, antifungal, and antiviral properties [23].

Therefore, due to the importance of calamondin and the fact that there has not been published data on calamondin peel essential oils as well as the optimization of extraction conditions or in-depth research on the kinetics of the process, this study was conducted to address this issue. First, by modeling the extraction process, the study described the mechanism of extracting essential oils by the hydro-distillation method based on the experimental results of the process. Building a kinetic model of the process helps to predict the amount of essential oil remaining in the plant material and to determine the extraction conditions for obtaining the highest amount of essential oil. Secondly, at the optimal points of the extraction, calamondin peel essential oil is assessed for quality based on the analysis of the chemical compositions of the essential oil, thereby providing the basis for further research on both optimization and mechanism and diversifying products from calamondin peel oil.

EXPERIMENTAL SECTION

Sample preparation

Fresh calamondin (*Citrus microcarpa)* used in this research was obtained from Ben Tre province (latitude 10º14'54"N and Vietnamese longitude 106º22'34"E) in June of 2020, and was washed to remove all dirty particles. The samples were carefully peeled off with the help of a sharp razor blade. Materials were stored in a cool room (4ºC) and prepared for subsequent experiments.

Extraction of essential oil

Essential oil from calamondin peels was extracted by hydro-distillation using a modified Clevenger device with the following procedure: 100 g of Calamondin peels was ground and subjected to a hydro-distillation system, then included with the preliminarily determined amount of water. The solution extract was heated to produce a vapor mixture of essential oils and then liquefied at the condensate. The resulting essential oil (upper layer) and water (lower layer) at Clevenger are shown in Fig. 1.

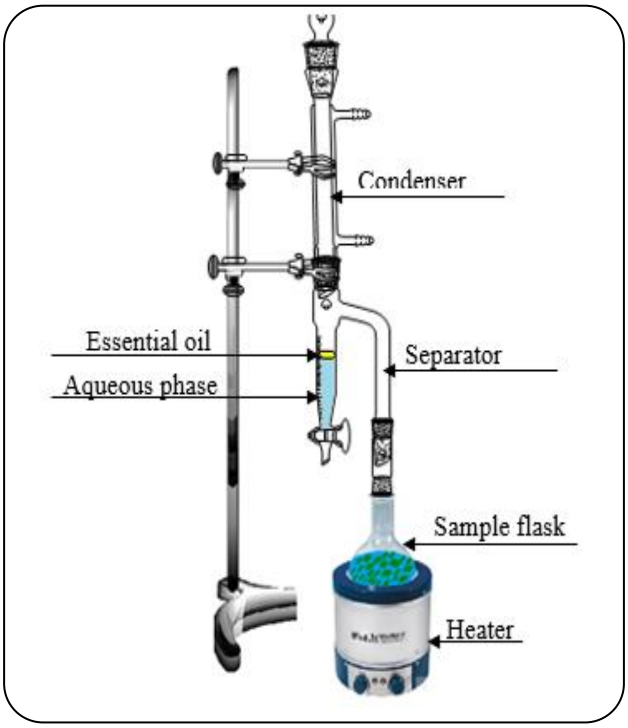

Fig. 1: Hydro-distillation Clevenger apparatus system.

In Fig. 1, the flask containing the materials and the water was heated by the heater. The mixture of essential oils and water obtained after the extraction process was obtained from the Clevenger instrument (left) which can determine the volume of essential oils. The extraction process was optimized with water to the material ratio (1: 2, 1: 3, 1: 4 mL/g) and heating capacity (170W, 204W, 238W).

After the extraction process, the obtained calamondin essential oil was carefully collected, dehydrated with Na_2SO_4, stored at 4ºC temperature, and prepared for the Gas Chromatography-Mass Spectrometry analysis. Each experiment was performed three times with the best values reported as the final results.

The yield of the extraction process was calculated using equation (1):

$$Y = \frac{V \times 100}{W} \quad (1)$$

Where *Y* is the yield of the extraction process (%, v/w), *V* is the volume of essential oil obtained (mL), and *W* is the weight of calamondin peels used (g)

Analytical procedures

Compositions of obtained essential oils were determined by Gas Chromatography-Mass Spectrometry (GC-MS). First, a 25 µL sample of essential oil was introduced into 1.0 mL of n-hexane. The instrument was GC Agilent 6890N Gas Chromatograph MS 5973 inert with HP5-MS column. The pressure of the column was 9.3 psi. Carrier gas was He. The flow rate was 1.0 mL/min. The injection volume and temperature were 1.0 µL and 250 °C, respectively. The split ratio was 1:100. Temperature progress of the instrument was programmed as follows: 2 min of 50 °C, followed by an elevation to 80°C at 2°C/min, then to 150 ℃ at 5°C/min, then to 200°C at 10°C/min and then to 300 °C at 20°C/min, which was hold for 5 min.

Kinetic model

Kinetic modeling was used to assess the changing conditions that affect the extraction process of essential oils. Kinetic modeling not only provides a basic understanding of the process but also helps to control and check the process. Kinetic research is a fundamental step to effectively evaluate the extraction process. In this study, we used Origin 9.0 to find the parameters of linear regression. The non-stationary diffusion model and the first-order kinetic model were compared with the purpose of finding a suitable kinetic model, describing the extraction of essential oils by hydro-distillation method, and assessing the influencing factors of the extraction process.

Non-stationary diffusion model

The transport of essential oil from the plant material during the hydro-distillation process generally follows the unsteady-state diffusion. It was previously shown that the non-stationary diffusion model could be appropriately applied to describe the batch distillation processes including non-chemical reaction stages: washing and diffusion [24]. This implies that the essential oil diffusion through plant material is an unsteady-state process. The model could be described as follows.

$$\frac{q_o - q}{q_o} = (1 - b).\, e^{-kt} \quad (2)$$

where q is the yield of Calamondin essential oil obtained at time t (%v/w, mL/g), q_o is the initial average concentration of essential oil in the materials (%v/w, mL/g), and e is a constant. b represents the fast oil distillation (washing) stage and, k, characterizes the slow oil distillation (diffusion) stage. The model assumes four main assertions: uniform and isotropic plant particles, pseudo-component nature of essential oil, even distribution of essential oils in the cells, constant effective diffusion coefficients on materials and instantaneous washing of essential oil from the surface, leaving zero essential oil concentration during hydro-distillation.

Model of pseudo-first order kinetics

To accommodate the washing stage to the first-order kinetic desorption model, the intra-particle diffusion was taken into account with some assumptions [25-26]. First, the distribution of essential oil is assumed to be uniform within a material matrix. Second, the essential oil is absent on the matrix surface at the beginning of the extraction. Third, plant materials are assumed to be isotropic in size and shape, and the essential oil quantity is equal in plant materials.

Thus, the model for a spherical matrix of uniform size is the equation.

$$\frac{q}{q_o} = 1 - e^{-kt} \tag{3}$$

where q is the yield of Calamondin essential oil obtained at time t (mL/g), q_o is the initial average concentration of essential oil in the materials (mL/g), and k is the first-order rate constant (min^{-1}).

RESULTS AND DISCUSSION

In this study, the essential oil of calamondin peel was extracted by hydrodistillation with Clevenger device, a highly proposed method of extracting Citrus essential oils. The extraction process was influenced by the water-to-material ratio, heating power, and extraction time. Therefore, in order to obtain the best yield for the process, determining the influence of parameters on the extraction process is a necessary step. In addition, two kinetic models as: non-stationary diffusion and first-order kinetic models were compared to find a suitable model explaining the extraction mechanism of the process. Moreover, the quality of the essential oil from calamondin peels was determined using GC-MS.

Power

During the extraction process of hydro-distillation, power is considered one of the main factors affecting the essential oil yield. The lower limit of power for experiments is the lowest (i.e.170W) but ensures that the water can reach its boiling point. On the other hand, the upper limit of power for experiments is the maximum power (i.e. 238W), which there is no detrimental effect on the amount of collected essential oil or the quality of the essential oil. Therefore, a change in the amount of calamondin peels essential oil for 90 min was observed within the mentioned power range (170, 204, and 238 W), while the ratio of water and material was fixed at 3:1 mL/g (recommended by previous research on Citrus oil [27-28]), shown in Fig.2.

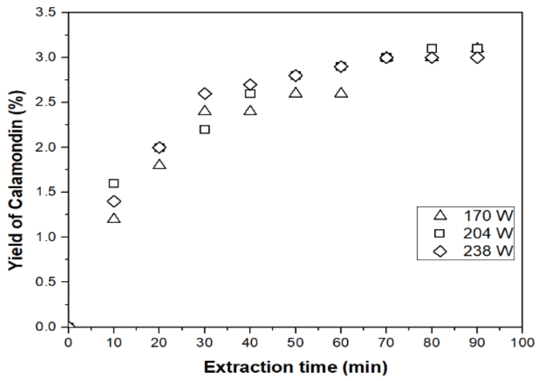

Fig. 2: The amount of extracted calamondin peels oil at different heating powers (constant ratio water and materials of 3:1 mL/g).

The results showed that a change in power led to a change in the extraction rate of the process. At a higher power, the amount of essential oil yielded more than that at the lower power. For instance, the highest amount of essential oil extracted for 30 min at 238 W was 2.6% which was higher than those at 204 W (2.4%) and 170 W (2.3%). Further extraction time was found to mostly be unchangeable, shown in Figure 2. In general, the essential oil yield over time extracted at the minimum power (170 W) was always lower than those at the power level of 204 W and 238 W. This was due to the heat transfer that is related to the steam flow rate of the process. The slow heat transfer did not show the effectiveness in steam formation, resulting in incomplete extraction; thus, the amount of essential oil still remained in the raw material, causing low extraction efficiency [29].

From Fig. 2, the results showed that the extraction yield at different power (170, 204, 238W) was almost the same at 70 min (yield of 3.0%). However, an extended extraction time (> 70 min) at high power (i.e. 238 W) was found to lower the extraction efficiency. Explaining this, essential oils contain volatile and heat-sensitive compounds that are rapidly decomposed when exposed to heat [28, 30].

Water and material ratio

Another important parameter affecting hydro-distillation is the water and materials ratio, which is the amount of water per amount of calamondin peels (mL/g). Based on previous studies on essential oils of fruit peels [27, 30], the best ratio of water and material is usually 3:1 mL/g, the range of water ratios for experiments was determined based on the data mentioned above. In addition, the lower and upper limits of the water ratio (2:1 mL/g and 4:1 mL/g) were established to prevent materials from being burnt when insufficient water or water spills out from the flask when excess water. As a result, the optimal condition for the extraction process was selected at the applied heating power of 204 W for 90 min. As expected, the upper and lower limits of water to materials ratio resulted in lower essential oils yield (i.e. 2: 1 mL/g and 4:1 mL/g) than the middle limit (i.e. 3:1 mL/g), depicted in Figure 3. For a lower water-to-material ratio (2:1 mL/g), the process yield was 3.5%. This was because the lower water content resulted in a large amount of heat on the sample, causing a decay of material. For a larger amount of water (i.e. 4:1 mL/g), this amount of water is wasted as it provided mostly heating energy for the extracting medium rather than the sample. The low yield for these effects can be explained by the hydrolytic effect [30].

As observed previously, experiments need to have a sufficient amount of water to protect the sample, avoiding wastage and the adverse effects of water. According to the results of the study, the appropriate amount of water for the extraction process was 300 mL of water in 100 g of calamondin peels (ratio of 3: 1 mL/g), tackling the mentioned issues and achieving the highest efficiency for the extraction process.

Extraction time is the most important factor in the extraction process. The extraction time must be long enough to obtain the maximum amount of essential oil from the plant material, depending on the plant material and the extraction method. The extraction time of the hydro-distillation of calamondin peels was determined from the beginning of the extraction process until the essential oil reached the saturation stage (Figure 2, 3). As observed, the amount of calamondin essential oil increased to the highest yield of 4.2% over a period of 80 min under the influence of investigated parameters during the extraction process. Since, the yield of calamondin essential oil did not further increase after 80 min, thus the extraction process was considered to be carried out for 80 min.

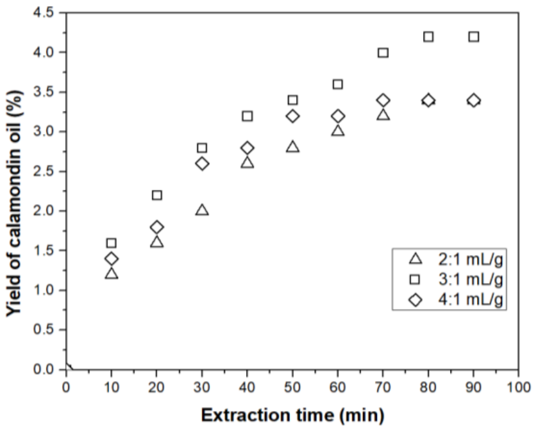

Fig. 3: The amount of extraction calamondin peels oil different water to material ratio (constant heating power of 204 W).

Kinetic model

As mentioned earlier, until now, data on kinetic research and optimization of essential oil extraction process from calamondin peels by hydro-distillation method have not been found. Therefore, this study was based on the extraction mechanism of the process to evaluate the experimental data using the first-order kinetic model and non-stationary diffusion model.

Calamondin essential oil yield over time was observed at different applied power levels such as 170, 204, and 238 W (Figure 2) and water-to-material ratios of 2: 1, 3: 1, 4: 1 mL/g (Figure 3). As depicted in Figures 2 and 3, the amount of essential oil increased with time. The kinetic models and mechanism of the extraction process were performed using linear equations of Equation 2-3 over time as shown in Figure 4-7 and based on which to calculate the kinetic parameters of the extraction process (Tables 1 and 2).

As observed from Figure 4-7, the linear form of the factors showed that the distribution points of the experimental data were closer to the non-stationary diffusion kinetic model than to the first-order kinetic model. The data points were at the upper limit of power (238W) and water-to-material ratio (4:1 mL/g), which appeared to be less distributed in the other ranges when observed in the first-order kinetics model. This did not seem to affect the non-stationary diffusion model,

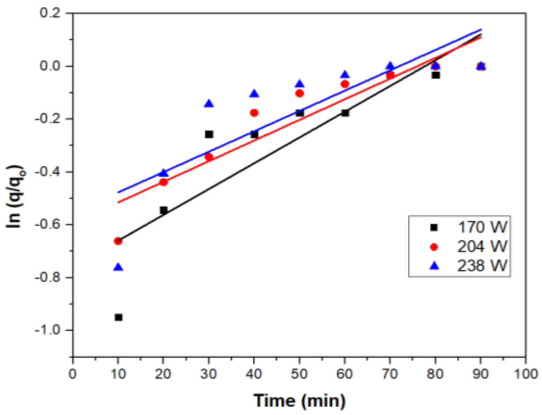

Fig. 4: First-order kinetic model of extraction calamondin peels oil by hydro-distillation at various heating power.

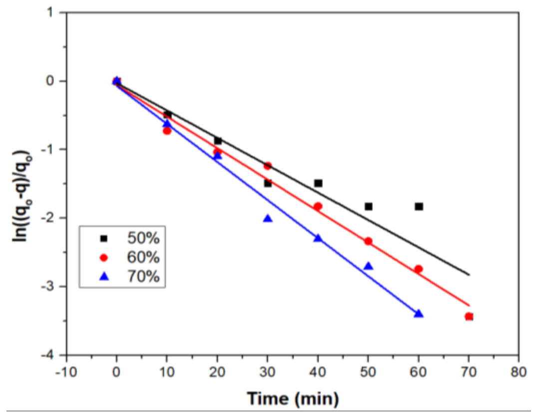

Fig. 6: Non-stationary diffusion kinetic model of extraction calamondin peels oil by hydro-distillation at various heating powers.

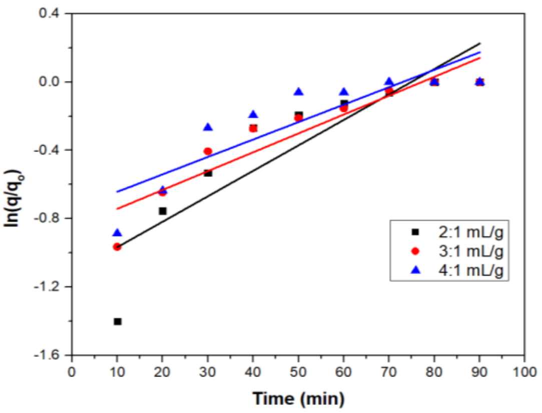

Fig. 5: First-order kinetic model of extraction calamondin peels oil by hydro-distillation at various water-to-material ratio.

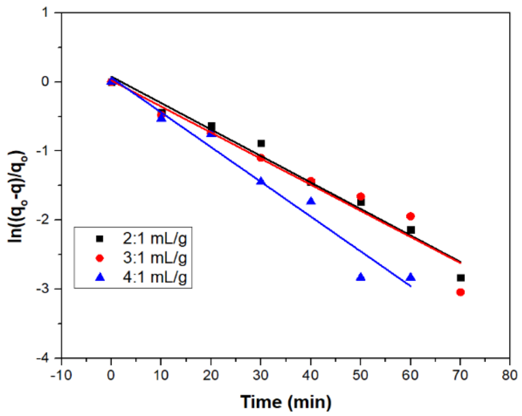

Fig. 7: Non-stationary diffusion kinetic model of extraction calamondin peels oil by hydro-distillation at various water-to-material ratio.

which was poorly distributed under extraction conditions such as 170 W and 3:1 mL/g. By visualizing this data in Table 1 and 2, the R^2 coefficients of the non-stationary diffusion kinetic model were greater than 0.85 under studied conditions. Meanwhile, the R^2 coefficients in the first-order kinetic model were in the range between 0.63 and 0.85. Therefore, the non-stationary diffusion kinetic model was consistent with the experimental data of the process, two conclusions can be drawn. First, the extraction mechanism of the process was described by the model's two-parameter model (b and k) through plant tissues. Secondly, the kinetic model of the extraction process was expressed through two stages: washing and diffusion [9, 24, 25].

As indicated in Figures 2 and 3, during the initial stage (fast oil distillation), the yield of oil increased rapidly. However, the oil yield increased slightly in the later stage (slow oil distillation stage) until a constant yield was reached. This was in line with previous findings implying that the washing stage is characterized by quick improvements in yield at the initial periods and the later diffusion stage refers to the process in which essential oils move outward the material surface and are then subjected to distillation, resulting in a slower increase in oil yield [9, 24].

As can be seen from Tables 1 and 2, the kinetic parameter (i.e. b and k) of the non-stationary diffusion kinetic model increased with the increase in extraction conditions such as power (from 170 to 204 W) and water-to-material ratios (from 2:1 to 4:1 mL/g). The results showed that at higher powers and water-to-material ratios, essential oils from calamondin peels were washed and diffused more easily. This was possibly due to the

Table 1: Values of kinetic parameter for different power.

Power (W)	Non-stationary diffusion model					First-order model			
	k(min^{-1})	b	R^{2*}	RSS^{a*}	SES^{b*}	k(min^{-1})	R^{2*}	RSS^{a*}	SES^{b*}
170	0.040	0.0280	0.86663	0.86632	0.00586	0.010	0.7401	0.16821	0.0020
204	0.046	0.0568	0.98358	0.12663	0.00224	0.008	0.8406	0.05942	0.0012
238	0.056	0.0662	0.98511	0.10875	0.00279	0.008	0.6304	0.17021	0.0020

Table 2: Values of the kinetic parameter for different ratio of water and material.

Ratio (mL/g)	Non-stationary diffusion model					Frits order model			
	k(min^{-1})	b	R^{2*}	RSS^{a*}	SES^{b*}	k(min^{-1})	R^{2*}	RSS^{a*}	SES^{b*}
2:1	0.038	-0.081	0.97606	0.12939	0.00227	0.015	0.75066	0.37260	0.00298
3:1	0.038	-0.022	0.93912	0.3299	0.00362	0.011	0.84600	0.11373	0.09260
4:1	0.05	-0.064	0.95846	0.25411	0.00426	0.010	0.73401	0.18982	0.00213

increased diffusivities and enhanced driving forces between essential oil and extracting medium.

The kinetic parameters of the process include fast and slow distillation coefficients (b and k) and these parameters are influenced by the extraction conditions of the extraction process. The non-stationary diffusion model was chosen to explain the extraction process. The mechanism of the extraction of the essential oil from calamondin peel consists of two parts: washing the essential oils from the peel surface of the material (fast distillation stage) and the diffusion of essential oils from the tissues to the surface of the material peels. Based on the extraction mechanism of the process, distillation can be described mathematically using the non-stationary diffusion model through plant material. The power of the process was observed to effectively improve the rapid distillation of essential oils through calamondin peels rather than diffusion. In particular, the fast distillation coefficient (b) increased from 0.028 to 0.0662 when the power increased to 238W, this parameter experienced an abnormal increase with the fast distillation constant. In addition, an increase in the water-to-material ratio also led to an increase in the kinetic parameters of the process (k and b). Therefore, the ratio of water and materials was not considered to be a noticeable factor affecting the extraction process compared to the extraction power. This was consistent with a previous study done by *Stojanovi et al.* [24]. In general, the higher the extraction parameters increased (both power and water-to-material ratio), the faster the distillation rate of the process obtained. However, when it reached a certain threshold, it was found to reduce the efficiency of the extraction process. Therefore, the extraction conditions must be determined appropriately to avoid the adverse effects of the extraction factors on the performance and quality of the essential oil.

The result of GC-MS

Calamondin peel oil was extracted under optimum conditions (power of 204 W, water-to-material-ratio of 3:1 mL/g, and extraction time of 80 min) with 4.2% yield (v/w) and the chemical composition was characterized by GC-MS. In calamondin peel essential oil, a total of 15 components were determined and their relative proportions are presented in Table 3. Compounds were determined by comparing the retention time and mass spectra of the sample with the standard spectrum library. Most of the ingredients were terpene, especially monoterpene and sesquiterpene. The most common peak in the chromatogram of the calamondin peels oil was at the retention time of 11.862 min (Figure 8), which accounted for the highest concentration of limonene (88.637%), followed by Germacrene D (4.451%), β-Edudesmol (1.034%). According to data from Table 3, the major compounds in calamondin essential oils were monoterpenes hydrocarbons, including limonene (88.637%), β-Myrcene (0.779%), β-Pinene (0.38%), 1R-α-Pinene (0.292%) which represented 90.088% of the total essential oil. The sesquiterpene contents were observed to be 5.462% of the total calamondin essential oil, mainly with Germacrene D (4.451%).

Table 3: Chemical composition of essential oil from calamondin peels.

Peak	R.T	Compound	Formula	Percent
1	7.230	1R-α-Pinene	$C_{10}H_{16}$	0.292
2	9.039	β-Pinene	$C_{10}H_{16}$	0.38
3	9.907	β-Myrcene	$C_{10}H_{16}$	0.779
4	11.862	D-Limonene	$C_{10}H_{16}$	88.637
5	26.481	Delta-Elemene	$C_{15}H_{24}$	0.435
6	28.06	Geranyl acetate	$C_{12}H_{20}O_2$	0.347
7	28.217	β-Elemen	$C_{15}H_{24}$	0.265
8	30.800	Germacrene D	$C_{15}H_{24}$	4.451
9	30.936	β-Selinene	$C_{15}H_{24}$	0.352
10	31.218	Bicyclogermacren	$C_{15}H_{24}$	0.394
11	32.494	Elemol	$C_{15}H_{26}O$	0.834
12	33.926	undetermined		0.122
13	34.136	γ-Eudesmol	$C_{15}H_{26}O$	0.842
14	34.460	β-Edudesmol	$C_{15}H_{26}O$	1.034
15	34.512	α-Eudesmol	$C_{15}H_{26}O$	0.835

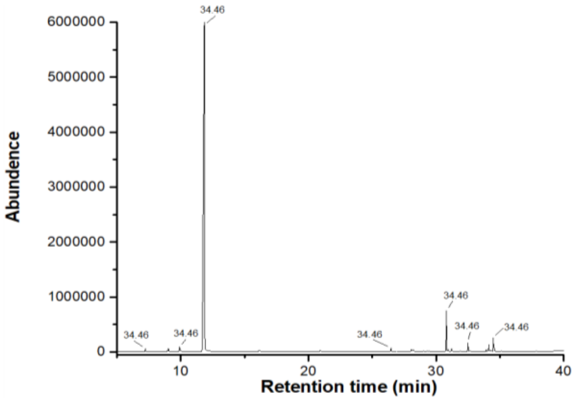

Fig. 8: GC-MS of the essential oil of calamondin peels by hydro-distillation.

Limonene (the main compound of essential oils) has been reported as an insecticide that is toxic to fleas and may play a role in resisting insect attacks. Limonene is commonly utilized as a dietary supplement, flavoring ingredient for cosmetic products, and reagent in the manufacture of polymers and adhesives [32]. *Negro et al*. [33] showed the extraction of key components such as D-Limonene from orange peels (Citrus trees) at the best extraction conditions of 130oC which is consistent with the heat in this study. Another useful compound is β-Myrcene which is an olefinic natural organic hydrocarbon. According to *Arno Behr* and *Leif Johnen* [34], Myrcene is a natural chemical in sustainable chemistry. Moreover, Myrcene is an important intermediate used in the perfume industry. In addition, α-Pinene is considered an anti-inflammatory and antimicrobial agent [34]. Besides, the component stands out in oil, terpene esters (geranyl acetate) could impart fresh, fruity, and green notes. *Manuel G. Moshonas* and *Philip E. Shaw* [15] published the chemical composition of calamondin peels essential oil in which limonene (91%) was the main constituent followed by β-Pinene (1.36%). This component was also found in the study of L. Cuevas-Glory et al. [36]. Limonene and Myrcene extracted by hexane solvent accounted for 77% and 4.2%, respectively. In addition, *Cheong et al*. [37] extracted the essential oil with a hexane solvent and the components of calamondin essential oil were Limonene, myrcene, β-pinene, linalool and α-pinene. The composition of volatile compounds in essential oils can be affected by environmental factors, extraction method, and the geographical characteristics of the area.

CONCLUSIONS

In this study, the kinetic model of the hydro-distillation extraction of calamondin peel essential oil was used to describe the experimental data and the optimal extraction conditions of the process in which the extraction process obtained the maximum amount of essential oil with minimum time. The results showed that the non-stationary diffusion model consisted of two parameters of washing and diffusion stages that better described the extraction process at all operating conditions. Both conditions such as power and water-to-material ratio affected the extraction time, kinetic parameters, and the extraction yield. In particular, the power level was considered a primary factor that decided the extraction process. The efficiency of the process reached 4.2% under extraction conditions such as an applied power of 204 W, a water-to-material ratio of 3:1 mL/g, and an extraction time of 80 min. In addition, calamondin peel essential oil quality was also presented in GC-MS analysis. 15 compounds found in calamondin essential oil in which limonene, germacrene-D, and β-Edudesmol were the most predominant compounds.

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