The Kinetic Model of Essential Oil Hydrodistillation from Turmeric (Curcuma longa)

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Abstract. Turmeric is commonly used as a spice, food preservative, coloring agent, and medicine. Turmeric essential oil (EO) is effective in acne treatment, skin lightening, anti-aging, analgesic, and anti-inflammatory. In this study, the kinetic model evaluates variable conditions that affect the hydrodistillation (HD) process. The HD method was chosen because it is easy for industrial-scale applications. The significant HD parameters, including turmeric-water ratio (TWR), heating oil temperature (HOT), and distillation time, were investigated. The highest yield (6.72%) was achieved under the following conditions: the turmeric-water ratio of 1:5, heating oil temperature of 150°C, and distillation time of 4 hours. There have been no studies on the kinetic model of essential oil extraction from turmeric by hydrodistillation. Therefore, three kinetic models were proposed to test for compatibility. The results showed that the two-site desorption model had a better fit than other models. The TWR and HOT had a more significant impact on the cell and tissue alteration of oil glands than the diffusion of essential oil.

1. Introduction
Turmeric (Curcuma longa) is commonly used as a spice, food preservative, coloring agent in India, China, and Southeast Asia. Thousands of years ago, it was also used as a medicine in traditional medicine. Turmeric's components have been studied in many researches. The bioactive compounds in turmeric are Turmerone, ar-Tumerone, and 2-Methyl-6-(4-methylenecyclo) [1]. The volatile essential oil extracted from rhizomes showed an antioxidant potential [2]. Turmeric has been used to remedy various diseases such as biliary disorders, anorexia, cough, diabetic wounds, hepatic disorders, rheumatism, and sinusitis [3].

The essential oil from cherry laurel (Prunus laurocerasus L.) leaves was isolated by hydrodistillation in a Clevenger-type apparatus. A simplified diffusional model described the kinetics of hydrodistillation. It is a two-parameter model, where one parameter, b, characterizes the fast oil distillation or oil (washing) stage (the so-called quick distillation coefficient), and the other, k, indicates the slow oil distillation stage (the so-called slow distillation coefficient). The fact that the intercept of the assumed relationship is zero means that only diffusion of the oil through plant particles towards their external surface limits the overall process rate. There was no "essential oil washing" at the beginning of the hydrodistillation [4]. The microwave steam diffusion (MSD) was compared with conventional steam diffusion (SD) to extract orange peel essential oil. Cytohistological investigations using light microscopy provided evidence for rapid and pronounced cell and tissue alterations of oil glands with MSD compared to SD. The first-order kinetic model's values of extraction kinetics agreed with the actual experimental values [5]. The kinetic of essential oil recovery from lemongrass was investigated using an experimentally validated first-order kinetic model. This model neglected oil diffusion resistance from the plant tissues to the leaf surface. The integral method of analysis was used to test the fit of the model...
to the experimental results. The straight lines obtained indicated that the recovery of essential oil from lemongrass followed first-order rate kinetics with a mean rate constant, k, of 0.0451. It was observed that oil extraction was not instantaneous as some time was required to wet the plant material to diffuse the oil from within the leaves to the surface [6].

The kinetic model of microwave-assisted hydrodistillation (MAHD) of juniper berry essential oil was investigated. The results showed that MAHD and HD are the same and include fast (washing) and slow (diffusion) distillation that co-occurs [7]. The patchouli extraction showed it consisted of a fast distillation, followed by a slow one. Based on experimental values, a semi-empirical model was fitted. The results showed that the distillation time for MAHD was shorter than HD. This could be due to a higher extraction rate by microwave and both mass and heat transfer phenomena acting in the same way [8]. The essential oil from lemongrass leaves was extracted using microwave radiation and hydrodistillation. The distillation time was found to be the parameter that most influences the process. Fit data for the desorption model has been implemented. The results showed that MAHD is a better alternative to HD in yield, distillation time, energy efficiency, biological activity, and environmental friendliness [9].

The kinetic model of fennel essential oil extraction was also determined for MAHD and HD method. The composition of essential oil obtained by HD and MAHD is similar. The modified Clever apparatus is appropriate to get kinetic data of hydrodistillation processes independent of the heating method. The proposed semi-empirical model fitted both HD and MAHD processes [10]. The kinetic of Aquilaria malaccensis leaves HD was modeled by both pseudo-first-order kinetic and non-stationary diffusion models (simultaneous washing and diffusion). The results indicated that the non-stationary diffusion model better describes the HD mechanism of the essential oil. The optimum parameters were a time of 3 hours, a solid-liquid ratio of 1:10 (g/ml), the heating power of 300 W, and a yield of 0.05 v/w. The essential oil is yellow and has a strong smell [11].

Although there are many studies on HD and MAHD methods in various plants, there is not much research on turmeric. There have been no studies on the kinetic model of essential oil extraction from turmeric by hydrodistillation. Therefore, this work aims to determine the HD process parameters and develop a kinetic model suitable for experimental data. This research helps understand the mechanism of HD clearly and assess variable conditions affecting the HD process.

2. Materials and methods

2.1. Materials
Turmeric was purchased from a local supplier in Ba Ria - Vung Tau province, Vietnam. Over 1-year-old, fresh and non-pest turmeric were selected. They were stored in a fridge (4°C) for subsequent experiments. Sodium sulfate (99% purity) was used to anhydrous essential oil, made in China.

2.2. Hydrodistillation process
First, turmeric was washed, peeled, and cut into slices of 5 mm. The initial moisture content of sliced turmeric was measured. 200 g of sliced turmeric was pured with the surveyed amount of water. The mixture is then charged into a flask for distillation. The distillation equipment was heated by cooking oil. Distillation time is the period elapsed since the first liquid drop condensed. The volume of EO was read every 30 minutes. When the volume obtained did not change, EO and condensate were separated. Then the crude EO was made anhydrous with sodium sulfate. Finally, the mixture was filtered to obtain pure EO. The significant HD parameters, including turmeric-water ratio, heating oil temperature, and distillation time, were investigated. The following expression determined the distillation yield:

\[
yield = \frac{Vd}{m(1-X)}
\]

Where V (mL) and d (g/mL) are the volume and density of EO, respectively; m (g) and X are the mass and moisture content of sliced turmeric, respectively. The density of EO was determined by the Pycnometer method. The Ohaus MB45 moisture analyzer determined the moisture content of turmeric.
2.3. The kinetic models of hydrodistillation

The kinetic model is used to evaluate variable conditions that affect EO hydrodistillation. In this study, we investigated the variation of distillation yield overtime at different TWRs and HOTs. Statistical Product and Services Solutions (SPSS) software was utilized to find the nonlinear regression equation's parameters by minimizing the sum of standard error (SSE) between the experimental and predicted value. The kinetic models were compared to find a suitable kinetic model, which describes the process of turmeric EO hydrodistillation.

2.3.1. The one-site desorption model. The one site desorption model does not include the stage of breaking EO particles from plant cells (washing). It is suitable to describe the diffusion process of EO particles [9,11].

\[ \frac{q}{q_0} = 1 - e^{-kt} \]  

(2)

Where q is the yield after time t; qo is the maximum yield; k is the first-order rate constant (min⁻¹).

2.3.2. The two-site desorption model. The two-site desorption model includes two stages of breaking EO particles from plant cells and diffusing EO particles [9]. The following equation represents this model.

\[ \frac{q}{q_0} = 1 - Fe^{-k_1t} - (1-F)e^{-k_2t} \]  

(3)

Where F and 1-F indicate the fraction of EO released quickly and slowly, respectively; k₁ and k₂ are the first-order rate constants (min⁻¹).

2.3.3. The non-stationary diffusion model. The batch distillation process without chemical reaction could be described by the non-stationary diffusion model based on the unsteady state EO diffusion through plant cells. This model consists of two consecutive stages: washing and diffusion [11,12].

\[ \frac{q_0 - q}{q_0} = (1 - b)e^{-kt} \]  

(4)

Or

\[ \frac{q}{q_0} = 1 - (1 - b)e^{-kt} \]  

(5)

Where b represents the slow EO distillation stage (washing), and k (min⁻¹) represents the fast EO distillation stage (diffusion).

3. Results and discussion

3.1. Effect of turmeric-water ratio

Figure 1 shows the effect of the turmeric-water ratio on distillation efficiency. The results showed that EO's yield increased with time, the highest yield obtained at the ratio of 1:5 (6.72%). In the distillation process, steam penetrates the epidermis, breaks the EO cells, and carries the EO. The lower yield at a ratio of 1:4 can be explained by the insufficient amount of water to break the cell structure and protect turmeric from charring and overheating [11]. Conversely, more water (i.e., 1:6 and 1:7) will dissolve the EO according to the hydrolytic effect [13]. Therefore, a ratio of 1:5 was selected for further surveys.
3.2. Effect of heating oil temperature

In this study, the system was heated by cooking oil. The variation of EO volume during 4 hours was observed at different HOTs (130, 140, 150, and 160 °C) while the turmeric-water ratio (1:5) was constant. The minimum HOT for the experiment was the lowest HOT, at which water could reach the boiling point. The influence of HOT on distillation yield is shown in Figure 2. The results indicated that at higher temperatures, the distillation rate was faster than at lower temperatures. The lowest yield was achieved at the minimum HOT, and the highest yield was achieved at medium HOT. Based on the Fourier rate equation for conduction and Newton rate equation for convection, the heat transfer rate is proportional to the temperature difference between the heating and flask [14]. Therefore at minimum HOT, the heat transfer rate between the surface and the core of the flask containing the sample and water is slower than at other HOTs [11].

On the other hand, a slower heat transfer may have influenced steam formation, resulting in incomplete distillation and lower yield. However, yield decreased when distilled at 160°C. This may be due to charring or decomposition of raw materials due to rapid heating and high temperature over a long period [11].

Figure 1. Hydrodistillation yield as a function of time at different turmeric-water ratios.

Figure 2. Hydrodistillation yield as a function of time at different heating oil temperature.
3.3. The kinetic models of hydrodistillation

Tables 1 and 2 show the computed parameters from three selected kinetic models at different TWRs and HOTs, respectively. The parameters included the first-order rate constant (k₁, k₂), and the EO fraction was released quickly (F, b). The coefficient of determination (R²) indicates the relationship between the independent and dependent variables. The higher R² is, the closer this relationship is.

**Table 1.** Parameters of the kinetic models at different turmeric-water ratios.

| TWR | one-site desorption model | two-site desorption model | non-stationary diffusion model |
|-----|---------------------------|----------------------------|--------------------------------|
|     | k (min⁻¹) | SSE | R² | k₁ (min⁻¹) | k₂ (min⁻¹) | F | SSE | R² | k (min⁻¹) | b | SSE | R² |
| 1:4 | 0.012 | 0.016 | 0.988 | 0.012 | 2.002 | 1.000 | 0.016 | 0.988 | 0.012 | 0.000 | 0.016 | 0.988 |
| 1:5 | 0.015 | 0.022 | 0.975 | 0.012 | 2.001 | 0.791 | 0.010 | 0.988 | 0.014 | 0.043 | 0.020 | 0.976 |
| 1:6 | 0.014 | 0.015 | 0.988 | 0.014 | 2.002 | 1.000 | 0.015 | 0.988 | 0.014 | 0.000 | 0.015 | 0.988 |
| 1:7 | 0.014 | 0.032 | 0.977 | 0.014 | 2.002 | 1.000 | 0.032 | 0.977 | 0.014 | 0.000 | 0.032 | 0.977 |

**Table 2.** Parameters of the kinetic models at different heating oil temperatures.

| HOT (°C) | one-site desorption model | two-site desorption model | non-stationary diffusion model |
|----------|---------------------------|----------------------------|--------------------------------|
|         | k (min⁻¹) | SSE | R² | k₁ (min⁻¹) | k₂ (min⁻¹) | F | SSE | R² | k (min⁻¹) | b | SSE | R² |
| 130      | 0.013 | 0.016 | 0.983 | 0.012 | 2.002 | 0.935 | 0.014 | 0.985 | 0.012 | 0.015 | 0.015 | 0.983 |
| 140      | 0.015 | 0.010 | 0.992 | 0.015 | 2.001 | 1.000 | 0.010 | 0.992 | 0.015 | 0.000 | 0.010 | 0.992 |
| 150      | 0.015 | 0.022 | 0.975 | 0.012 | 2.002 | 0.791 | 0.010 | 0.988 | 0.014 | 0.043 | 0.020 | 0.976 |
| 160      | 0.018 | 0.030 | 0.967 | 0.013 | 2.002 | 0.728 | 0.014 | 0.985 | 0.017 | 0.045 | 0.027 | 0.967 |

Tables 1 and 2 show that the coefficient k₁ varies with TWR and HOT, while k₂ is almost constant. The k₁ values in all models are slightly different. In the two-site desorption model, k₂ values are much larger than k₁ values. The coefficient F (approximately 1) indicates that the fraction of EO released quickly is larger than the rest. This may be due to the sliced turmeric being pureed before distillation, resulting in a more available EO release. Therefore, it can be concluded that TWR and HOT have more impact on stage 1 (washing) rather than to stage 2 (diffusion).

In stage 1, the plant particles are broken. This stage is characterized by a rapid increase in the amount of EO at the beginning of the distillation process. In stage 2, the distillation process slows down. During this period, the EO diffuses from the inside of turmeric to the outer surface and then escapes with steam. Stage 2 is characterized by a slow increase in the amount of EO until constant.

Figure 3 shows the kinetic models fit for HD under optimized conditions (TWR of 1:5 and HOT of 150°C). The results indicate that three kinetic models are relatively consistent with experimental data. They can be used for modeling of EO extraction from turmeric. The two-site desorption model has a higher correlation than other models. The higher R² (0.988) and lower SSE (0.010) indicate a better fit of this model for all different TWRs and HOTs. This could be due to raw material treatment (pureeing) significantly affected the HD process. Besides, when the F value reaches 0 or 1, the two-site desorption model becomes the one-site desorption model. Similarly, when b value reaches 0, the non-stationary diffusion model becomes the one-site desorption model.

Thereby, it can be concluded that the kinetic model for HD from turmeric is a three-parameter (F, k₁, k₂) model of unsteady-state diffusion through the plant particles, consisted of two stages of quick and slow release. The TWR and HOT have more impact on the fraction of EO released quickly than the fraction released slowly.
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4. Conclusion
In this study, turmeric EO was obtained by hydrodistillation method. The parameters that affect the distillation process, such as turmeric-water ratio, heating oil temperature, and distillation time, were investigated. The highest yield was 6.72% when distilled with pureed turmeric, the turmeric-water ratio of 1:5, heating oil temperature of 150˚C, and distillation time of 4 hours. The obtained essential oil is light yellow and has a characteristic aroma of turmeric. Three kinetic models of the distillation process were also proposed to check the suitability. The two-site desorption model had a better fit than other models. In particular, the essential oil was rapidly released. The material-water ratio and heating oil temperature had a more significant impact on breaking essential oil cells than the diffusion of essential oil.

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Figure 3. The different kinetic models fit for HD at TWR of 1:5 and HOT of 150˚C.
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