

Optimisation and Kinetics Studies on the Extraction of Essential Oil from *Zingiber Cassumunar*

Teoh Yi Peng, Mashitah Mat Don* and Muhammad Azhar Tahrel

School of Chemical Engineering, Universiti Sains Malaysia
Engineering Campus, 14300 Nibong Tebal,
Seberang Prai Selatan, Pulau Pinang, Malaysia

*Corresponding author: chmashitah@eng.usm.my / ita56@hotmail.com

Abstract: *Three operating parameters of hydrodistillation have been optimised by a response surface method using a central composite design to obtain high yields of essential oil from a rhizome of the Zingiberaceae species Zingiber cassumunar (Z. cassumunar). The optimal conditions for the maximum essential oil produced (6.64 g) were found to be an extraction time of 4 hr, a solid-to-solvent ratio of 3:150 and a hydrodistillation rate of 78 ml/hr. The study was subsequently continued with the three proposed models of the extraction process. Kinetics models proposed by Milojevi et al. and Hervas et al. were suitable for the process under low (20 ml/hr) and high distillation rates (70 ml/hr), whereas the model by Ana et al. was valid for all ranges of rates studied (20–70 ml/hr). It can be concluded that the hydrodistillation rate was one of the important parameters for determining the extraction kinetics.*

Keywords: *Zingiber cassumunar*, essential oil, optimisation, modelling, kinetics parameters

1. INTRODUCTION

Essential oils are the subtle, natural, aromatic and volatile compounds extracted from the flowers, seeds, leaves, stems, bark and roots of herbs. They are usually obtained through steam distillation or a hydrodistillation process.¹ Essential oils have become more significant in human life nowadays since their discovery thousands of years back. As time progresses, scientists have been discovering more and more benefits of essential oils, creating a significant increase in demand for them worldwide.

Essential oils have been largely employed due to their observed natural properties, which exhibit antibacterial, antiviral, antifungal, insecticidal and anti-herbivore characteristics. At present, approximately 3000 essential oils are known, 200 of which are commercially important, especially for the pharmaceutical, agronomic, food, sanitary, cosmetic and perfume industries.²

Generally, essential oils are extracted from various aromatic plants localised in temperate to warm countries, such as Mediterranean and tropical countries, where they represent an important part of the traditional pharmacopoeia.¹ Pithayanukul et al.³ studied the extraction of essential oil from *Zingiber* species, which is a well-known herb in Southeast Asia that has been used for centuries in Thailand and other countries in Southeast Asia as a folk medicine for the treatment of inflammation, sprains, muscular pain, wounds and asthma as well as a mosquito repellent. This essential oil exhibits antimicrobial activity against a wide range of gram-positive and gram-negative bacteria, dermatophytes and yeasts. Dermatophytes were found to be the most susceptible microorganisms followed by yeasts, whereas bacteria were the least susceptible. Tripathi et al.⁴ in their studies stated that essential oil extracted from *Z. cassumunar* was found to exhibit absolute fungitoxic activity. Meanwhile, the rhizome oil of *Z. cassumunar* Roxb. from Malaysia was found to exhibit high activity against yeast.⁵

Several extraction methods for extracting essential oils have been introduced by Bakkali et al.,¹ including the use of liquid carbon dioxide or microwaves and low- or high-pressure distillation using boiling water or hot steam. A hydrodistillation process for the extraction of essential oil from *Z. cassumunar* has been conducted by Bhuiyan et al.,⁶ in which 64 and 32 compounds were extracted from the leaf and rhizome.

Owing to the new attraction for natural products like essential oils, despite their wide and being familiar as fragrances, it is useful for developing, improving and optimising the process of extraction. Response surface methodology (RSM) is effective for responses that are influenced by many factors and their interactions, as was originally described by Montgomery.⁷ However, work on the optimisation of essential oil extraction from the Zingiberaceae species is less frequently reported. In fact, the kinetics of the extraction process is yet to be exploited. In the present study, hydrodistillation is used as the main method for the extraction of crude rhizomes of *Z. cassumunar*, and the working conditions including the extraction time, hydrodistillation rate and solid-to-solvent ratio are optimised by RSM to obtain the highest essential oil yield. The kinetics of the extraction process will also be investigated.

2. EXPERIMENTAL

2.1 Plant Materials

The raw material, *Z. cassumunar*, was obtained from Malim Nawar, Perak, Malaysia. The rhizome was ground and dried at 50°C prior to the extraction process.

2.2 Extraction Procedure

The hydrodistillation method was used for the extraction of the essential oil from the rhizome. A total of 3 g of rhizome was put into 500 ml round-bottom flask containing different volumes of deionised water (100, 150 or 200 ml). To study the hydrodistillation rate, the mixture was subsequently heated using a heating mantle by manipulating the power. Next, the extract was concentrated using a rotary evaporator at 90°C for 40 min. The concentrated essential oil obtained was weighed.

2.3 Experimental Design using RSM

RSM is a collection of mathematical and statistical techniques that are useful for the modelling and analysis of a problem in which a response of interest is influenced by several variables. The objective is to optimise the response.⁶ The RSM used in this study was a central composite face-centred design involving three different factors: extraction time, hydrodistillation rate and solid-to-solvent ratio. The extraction of essential oil from *Z. cassumunar* was assessed based on the face-centred experimental plan, as shown in Table 1. The results were analysed using Analysis of Variance (ANOVA) by Design Expert 6.0.6 software. Three-dimensional plots and their respective contour plots were obtained based on the effect of the levels of the three factors. From these three-dimensional plots, the simultaneous interaction effects of the three factors on the response were studied. The optimum region was also identified based on the main parameters in the overlay plot. The experiment was repeated five times randomly, and each result was compared with the predicted values to determine the model adequacy.

Table 1: Levels of the variable tested in the 2³ central composite designs.

Independent variables	Code	Range and levels				
		$-\alpha$	-1	0	+1	$+\alpha$
Extraction time (hr)	A	0.64	2	4	6	7.36
Hydrodistillation rate (ml/hr)	B	3.32	4	5	6	6.68
Solid to solvent ratio (g:ml)	C	4:100	3:100	3:150	3:200	1:100

2.4 Analysis Method

In this study, the essential oil obtained was analysed using gas chromatography mass spectrometry (GC-MS). The gas chromatography analyses were performed using a Perkin Elmer Clarus 600 gas chromatograph equipped with an ELITE-5 column. The gas chromatograph was coupled to the Perkin Elmer 600T mass spectrometer. The oven temperature was programmed at 65°C for 4 min and was increased to 280°C at a rate of 8°C/min.

2.5 Kinetics Model Proposed

2.5.1 Milojevi et al. (2008) method

The mechanism proposed to describe the hydrodistillation process of *Z. cassumunar* is similar to that presented by Milojevi et al.⁸ The mass transport of essential oil through plant particles during the hydrodistillation process occurs as unsteady-state diffusion. Thus, a batch hydrodistillation process involving no chemical reaction can be simulated using Fick's second law at unsteady state for one-dimensional rectangle geometry,⁹ as shown in Equation 1.

$$\frac{\partial q_p}{\partial t} = D_{\text{eff}} \frac{\partial^2 q_p}{\partial x^2} \quad (1)$$

where q_p denotes average concentration of essential oil at time t , x is the distance along the direction of diffusion, and D_{eff} is the effective diffusion coefficient.

The initial condition was

$$q_p = q_o \text{ at } t = 0$$

and the boundary condition was

$$q_p = q \text{ at } t = t$$

To solve Equation 1, the following assumptions at the level of plant particles in the suspension should be made:

- (a) the plant particles are isotropic and equal in size, shape and initial oil content. The particles do not change size and shape during the hydrodistillation;

- (b) the essential oil is considered to be a pseudo-component;
- (c) a portion of the essential oil is located on the external surfaces of the broken plant parts, and the rest is uniformly distributed in the plant particles;
- (d) the effective diffusion coefficient is constant;
- (e) the concentration of essential oil on the external surfaces of the plant particles at any moment during the hydrodistillation is zero because of its instantaneous "washing" from the surfaces; and
- (f) there is no resistance to the mass transport of essential oil from the external surfaces of the plant particles.

For simple geometrical cases, such as a slab, cylinder or sphere, the solution is as follows:

$$\frac{q_0 - q}{q_0} = A \cdot e^{-kt} \quad (2)$$

where q_0 is the essential oil present in the rhizomes, q is the essential oil produced at time t , A is a constant, and k is the kinetics constant, including the effective diffusion coefficient.

Further development involved the relationship between the hydrodistillation and the solvent extraction (from extractive substances in plant material) process. According to the solvent extraction model, there are two successive stages during the process: (i) "slow stage," i.e., the washing of essential oil from and near the external surfaces of the plant particles (theoretically at $t = 0$) and (ii) "fast stage," i.e., the diffusion of essential oil from the interior of the plant towards the external surfaces followed by its distillation. The first stage is characterised by a rapid increase in the oil present at the very beginning of the process:

$$\text{At time } t = 0, q = q_w \text{ and } \frac{q_w}{q_0} = b \quad (3)$$

where q_w is the essential oil produced at $t = 0$, and b is the relative amount of *Z. cassumunar* oil extracted at $t = 0$. The second stage is characterised by a slow exponential increase in the oil yield with the progress of hydrodistillation. By combining Equations 2 and 3, the basic kinetics equation for essential oil can be derived as follows:

$$\frac{q_o - q}{q_o} = (1 - b) \cdot e^{-kt} \quad (4)$$

The linearised form of the equation can be used to calculate the parameters of Equation 4 and is shown as:

$$\ln\left(\frac{q_o - q}{q_o}\right) = \ln(1 - b) - kt$$

The following assumptions are made for the *Z. cassumunar* oil mass balance for the hydrodistillation apparatus:

- (a) the pressure and temperature are constant in the apparatus;
- (b) the vapour condensation occurs only in the condenser;
- (c) the aromatic water is saturated by the hydrosoluble compounds of the essential oil;
- (d) the mass of water vapour in the flask, the connecting tube and the condenser and the mass of water in the condenser, the connected tube and the separator are much smaller than the mass of water in the flask;
- (e) the suspension in the flask is perfectly mixed; and
- (f) the flow of the vapour phase through the flask, the connecting tube and the condenser and the flow of the water condensate through the condenser, the separator and the connecting tube are plug flow.

2.5.2 Ana et al. (2007) method

In this study, the solid-liquid extraction kinetics proposed by Ana et al.¹⁰ was investigated, as shown in Equation 6:

$$C(t) = C_o + \frac{t}{K_1 + K_2 t} \quad (6)$$

where $C(t)$ is the weight of essential oil produced at time t , t is the extraction time in hours, C_o is the initial weight of essential oil at time $t=0$, K_1 is the extraction rate constant, and K_2 is the extraction capacity constant. Since C_o in all experimental runs was assumed to be zero, Equation 7 was used in the final form as:

$$C(t) = \frac{t}{K_1 + K_2 t} \quad (7)$$

The extraction rate constant K_1 is related to extraction rate (B_o) at the earliest time point ($t = t_0$),

$$B_o = \frac{1}{K_1} \quad (8)$$

The extraction capacity constant K_2 relates to the maximum of the extraction yield, i.e., the equilibrium concentration of the extracted essential oil (C_o). When $t \rightarrow \infty$, Equation 9 gives the relations between the equilibrium concentration and the K_2 constant,

$$C_o = \frac{1}{K_2} \quad (9)$$

Thus, the hydrodistillation rate coefficient can be written as in Equation 10:

$$k = \frac{K_2}{K_1} \quad (10)$$

2.5.3 Hervas et al. (2006) method

In addition, the kinetics mechanism proposed by Hervas et al.¹¹ was also used to study the extraction process under equilibrium conditions, as shown in Equation 11.

$$\frac{dC}{dt} = k(C_o - C) \quad (11)$$

where C is the weight of essential oil produced, t is the extraction time in hours, C_o the initial essential oil present, and k is the effective diffusion coefficient.

Integrating Equation 11 between the initial moment and a given point at time t gives rise to Equation 12.

$$C = C_o(1 - e^{-kt}) \quad (12)$$

For the data analysis, Equation 12 was linearised, as shown in Equation 13.

$$\ln\left(1 - \frac{C}{C_o}\right) = -kt \quad (13)$$

2.5 Model Validation

Model validation is possibly the most important step in the model building sequence.¹² In the present study, the simulation of the extraction kinetics of essential oil from *Z. cassumunar* was performed using an ordinary differential method with Polymath Computer Software Version 6.1. The ordinary differential equation was solved with the Runge-Kutta Fehlberg algorithm. The profiles from the simulation of the models and experimental data were subsequently evaluated using the mean square error (MSE) in which the calculated sum of squares errors divided by the length of the actual data period is shown in Equation 14.¹³

$$MSE = \left(\frac{\sum_{i=1}^{NT} (y_i - f_i)^2}{n_t} \right) \quad (14)$$

where f_i , y_i and n_t are the model data, experimental data and the length of the actual data period, respectively.

3. RESULTS AND DISCUSSION

3.1 Optimisation of Essential Oil Yield using RSM

A central composite design was used to develop a correlation between the extraction time, hydrodistillation rate and solid-to-solvent ratio to improve the essential oil yield. With multiple regression analysis, the polynomial equation with the coefficients of the full regression model equation and their statistical significance were determined and evaluated using Design Expert 6.0.6 software. The final model for essential oil produced in terms of coded values is presented in Equation 15. Based on this equation, the positive sign in front of the terms indicates a synergistic effect, while the negative sign indicates an antagonistic effect.⁷

$$Y = 1.74 + 1.19A - 1.26B + 357.15C - 0.078A^2 + 0.32B^2 - 2765.56C^2 - 0.19AB + 24.12AC - 53.5BC \quad (15)$$

where A, B, and C were coded values of the tested variables for extraction time, hydrodistillation rate and solid-to-solvent ratio, respectively. Table 2 presents the variations in the corresponding coded values of three parameters and the response based on experimental runs and predicted values proposed by the CCD design. The experimental essential oil produced from *Z. cassumunar* was in the range of

4.13 g to 6.82 g. The ANOVA for this model presented in Table 3 was significant ($P < 0.0005$) with a model F -value of 10.66.

Table 2: The coded variables, yield (experimental and predictive) and residuals for each run.

Std. order	Run	Coded variables			Essential oil produced		Residual
		A	B	C	Experimental (g)	Predictive (g)	
1	7	-1	-1	-1	4.13	4.09	0.04
2	12	1	-1	-1	4.24	4.17	0.07
3	14	-1	1	-1	5.18	5.17	0.01
4	15	1	1	-1	5.26	5.12	0.14
5	17	-1	-1	1	5.01	5.44	-0.43
6	18	1	-1	1	5.45	5.75	-0.30
7	3	-1	1	1	5.22	5.58	-0.36
8	6	1	1	1	5.43	5.76	-0.33
9	13	-1.682	0	0	4.96	4.66	0.30
10	19	1.682	0	0	4.98	4.87	0.11
11	2	0	-1.682	0	5.95	5.72	0.23
12	1	0	1.682	0	6.82	6.64	0.18
13	4	0	0	-1.682	3.57	3.86	-0.29
14	20	0	0	1.682	6.22	5.52	0.70
Repeated runs							
15	5	0	0	0	6.39	6.49	-0.10
16	10	0	0	0	6.42	6.49	-0.07
17	8	0	0	0	6.73	6.49	0.24
18	9	0	0	0	6.72	6.49	0.23
19	16	0	0	0	6.54	6.49	0.05
20	11	0	0	0	6.09	6.49	-0.40
Mean ^a					6.48	6.49	-0.05

Table 3 shows that the solid-to-solvent ratio (C) was highly significant compared with the extraction time (A) and the hydrodistillation rate (B). Although the extraction time and hydrodistillation were not significant terms, they cannot be eliminated if a hierarchical model is to be maintained. In contrast, (A^2) and (C^2) were much more significant compared to (B^2). The coefficient of variance (CV) is the ratio of the standard error of the estimate to the mean value of the observed response and is considered reproducible once it is not greater than 10%. In this work, the CV obtained was 7.13%. The "Adeq Precision" value

measures the signal-to-noise ratio. A ratio greater than 4 is desirable. From this experiment, a ratio of 9.908 was observed, which indicates an adequate signal. This model can be used to navigate the design space.

*Table 3: Analysis of variance (ANOVA) for the regression model of essential oil produced.

Source	Sum of Square	DF	Mean Square	F Value	Prob>F
Model	15.11	9	1.68	10.66	0.0005
A	0.06	1	0.06	0.35	0.5646
B	1.02	1	1.02	6.44	0.0294
C	3.34	1	3.34	21.22	0.0010
A ²	5.38	1	5.38	34.14	0.0002
B ²	0.18	1	0.18	1.12	0.3151
C ²	5.85	1	5.85	37.17	0.0001
AB	0.01	1	0.01	0.05	0.8215
AC	0.03	1	0.03	0.17	0.6906
BC	0.44	1	0.44	2.80	0.1249
Residual	1.58	10	0.16		
Lack of Fit	1.29	5	0.26	4.48	0.0627

*SD 0.40, C.V. 7.13, R^2 0.9056, adj R^2 0.8206, Pred R^2 0.8397, Adeq precision 9.908

The optimal condition with the highest yield of essential oil was chosen from a predicted condition proposed by the CCD design with the real model presented as:

$$\begin{aligned} \text{Essential oil produced} = & -6.18966 + 1.27745*\text{time} + 1.91343*\text{hydrodistillate rate} \\ & + 410.42537*\text{ratio} - 0.15271*\text{time}^2 - \\ & 0.11058*\text{hydrodistillate rate}^2 - 6373.75507*\text{ratio}^2 - \\ & 0.016250*\text{time}*\text{hydrodistillate rate} + 2.87500*\text{time}*\text{ratio} \\ & - 23.50000*\text{hydrodistillate rate}*\text{ratio} \end{aligned}$$

Table 2 also shows that the predicted optimum conditions for production of essential oil are 6.64 g, a hydrodistillation rate of 78 ml/hr, an extraction time of 4 hr and a solid-to-solvent ratio of 3:150.

Figure 1 represents the 3D plot of the extraction yield of essential oil based on interactions between the variables within the studied parameter ranges. As shown in Figure 1 [(a) and (b)], the extraction yield increased with increases in the extraction time of up to 4 hr. Beyond this point, the extraction yield remains constant or drops steadily. Similar findings have been reported by

Enujiugha and Akanbi¹⁴ using African bean oil seeds. Concurrently, the solid-to-solvent ratio factor also demonstrated the same trend as the previously described factors: the yield increased to a certain point (≈ 0.03 g solid/ml solvent) and subsequently started to drop when the ratio was further increased. As far as the essential oil present in the mixture is concerned, increasing the quantity of solvent will increase the concentration gradient of the interface between *Z. cassumunar* particles and the solvent (water). However, when all of the solute inside *Z. cassumunar* particles has been extracted, the quantity of solvent no longer changed the yield of the essential oil. This finding is in agreement with the study performed by Li et al.,¹⁵ who studied essential oil extraction from *Cuminum cyminum*. However, as observed from Figure 1 [(a) and (c)], the higher the hydrodistillation rate, the higher the production of essential oil. At a low hydrodistillation rate, the solvent had a higher residence time that was sufficient to allow penetration into the particles and that dissolved the solute from the tested plant species. At a higher hydrodistillation rate, the temperature became high, and the residence time decreased. Additionally, the higher temperature caused a decrease in viscosity and an increase in the diffusivity of solvent through the particles.¹⁵ Therefore, this effect led to higher essential oil production.

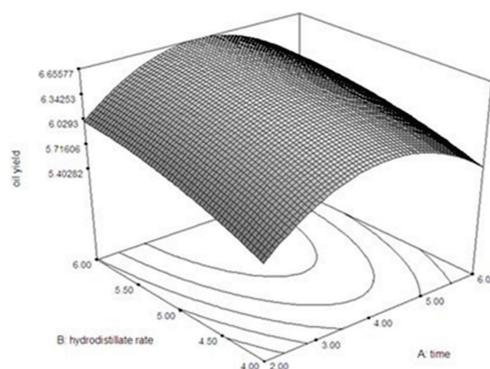


Figure 1: Response surface 3D and contour plot for the production of essential oil based on (a) effect of time and hydrodistillation rate, (b) effect of time and solid to solvent ratio, and (c) effect of hydrodistillation rate and solid to solvent ratio.

3.2 Optimum Range of the Parameters

A Design-expert plot illustrated the interaction between the three selected factors corresponding to the production of essential oil. The optimal conditions to obtain the maximal extraction (6.64 g) were a 4-hr extraction time, a hydrodistillation rate of 78 ml/hr and a solid-to-solvent ratio of 3 g:150 ml.

3.3 Verification Experiment

To validate the adequacy of the model, five sets of experiments were repeated randomly at optimum conditions to obtain a maximum production of essential oil. As shown in Table 4, the error between the experimental and predicted value was in the range of -0.33 to 0.45 . An experimental error of less than 1% indicated that the proposed model is adequate for obtaining an optimal value in the range of studied parameters.

Table 4: Validation of the data and model constructed.

Run	Essential oil produced (g)		Error (%)
	Experimental result	Predicted result	
1	6.43	6.64	-0.21
2	7.09	6.64	0.45
3	7.02	6.64	0.38
4	6.31	6.64	-0.33
5	6.80	6.64	0.16

3.4 GC-MS Analysis

The interpretation of the mass spectra obtained by the GC-MS method was conducted using the database of the National Institute of Standards and Technology (NIST). The spectrum of unknown components from the sample was compared with the spectrum of the known components stored in the NIST library version 2.0. In this study, 3-cyclohexen-1-ol, 4-methyl-1-(1-methylethyl), and terpinen-4-ol was found in the rhizome of *Z. cassumunar*, which is in agreement with the research performed by Bhuiyan et al.⁶ This chemical constituent played an important role in the antimicrobial activities of the essential oil.⁶

3.5 Kinetics of Essential Oil Extraction

3.5.1 Milojevi et al. (2008) method

Generally, kinetics parameter k increased with an increase in the hydrodistillation rate, whereas the kinetics parameter b showed a slightly decreasing pattern when the hydrodistillation rate was increased. The relationships of the kinetics parameters are as follows:

$$b = 0.423e^{-0.01HR}$$

$$k = 0.008e^{0.033HR}$$

where HR is the hydrodistillation rate, k is the slow distillation coefficient and b is the fast distillation coefficient.

The relationships between HR, k and b are obtained using the best-fit equation, as shown in Figure 2 [(a) and (b)]. By comparing these two graphs, it can be observed that the hydrodistillation rate affected the fast distillation coefficient much more than the slow distillation coefficient. These results implied that an increase in the energy input to the system contributed more effectively to the fast oil distillation as compared to the slow oil diffusion. This is due to the fact that the fast oil distillation is involved in the diffusion of solute (essential oil) from the external part to the outer part of the *Z. cassumunar* rhizome particles. On the other hand, the slow oil distillation rate is involved in the diffusion from the internal part of the plant particle to the external part and subsequently to the outer part of the particles.

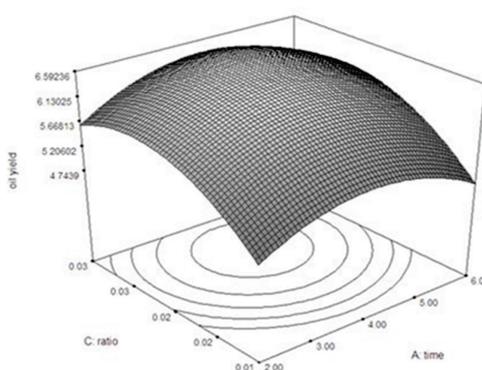


Figure 2: Kinetic parameter profile (a) b values and (b) k value for different hydrodistillation rate.

To determine that the proposed mathematical model is consistent with the experimental data, the profiles were plotted, as shown in Figure 3, and the MSE values were compared. The results showed that the experimental data fit well with the proposed mathematical model with lower MSE values determined to be less than 10% (Table 5), implying that the proposed kinetics model is valid in this experiment.

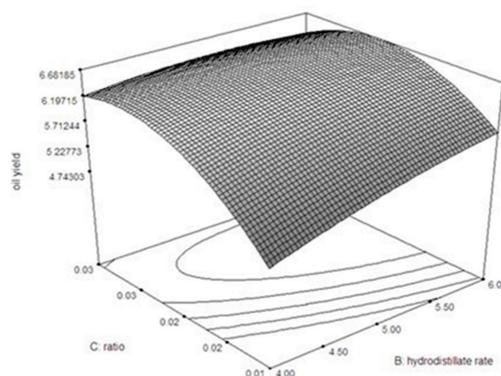


Figure 3. Validation of simulated value and experimental data of the extraction profile using Milojelvi et al. method.

Table 5: The production of essential oil, extraction kinetic parameter (k and b) and error analysis for the solid-liquid extraction by Milojelvi et al. method.

Hydrodistillation rate (ml/hr)	Essential oil produced (g)	k (hr^{-1})	b	MSE (%)
20	2.14	0.013	0.328	1.98
45	4.32	0.070	0.305	7.15
70	6.07	0.071	0.200	6.83

3.5.2 Ana et al. (2007) method

Table 6 showed the production of essential oil, the extraction constant and the coefficient (K_1 , K_2 and k) for the solid-liquid extraction using the method described by Ana et al.¹⁰ These results showed that the hydrodistillation rate was greatly influenced by the extraction kinetics of essential oil from the *Z. cassumunar* species. The values of the extraction rate constant (K_1) and the constant of extraction extent (K_2) showed a tendency to decrease with the increase in the hydrodistillation rate.

Table 6: The production of essential oil, extraction constant and coefficient (K_1 , K_2 and k) and error analysis for the solid-liquid extraction by Ana et al. method.

Hydrodistillation rate (ml/hr)	Essential oil produced (g)	K_1 (hr/g)	K_2 (g^{-1})	k (hr^{-1})	MSE (%)
20	2.14	0.255	0.567	2.224	1.81
45	4.32	0.084	0.232	2.762	2.49
70	6.07	0.058	0.165	2.845	1.11

Figure 4 shows the validation of simulated values and experimental data for the extraction profiles of essential oil from *Z. cassumunar* at different hydrodistillation rates. The kinetics model predicted the experimental data fairly well. By comparing the MSE values from Tables 5 and 6, it can be concluded that the Ana et al.¹⁰ values were lower than those of Milojelvi et al.⁸ Hence, it can be concluded that the kinetics model described by Ana et al.¹⁰ could be used for the extraction process with a wide range of hydrodistillation rates. Meanwhile, the latter method was suitable for the extraction process with a lower hydrodistillation rate (20 ml/hr), as it can be described in the fast and slow stages.

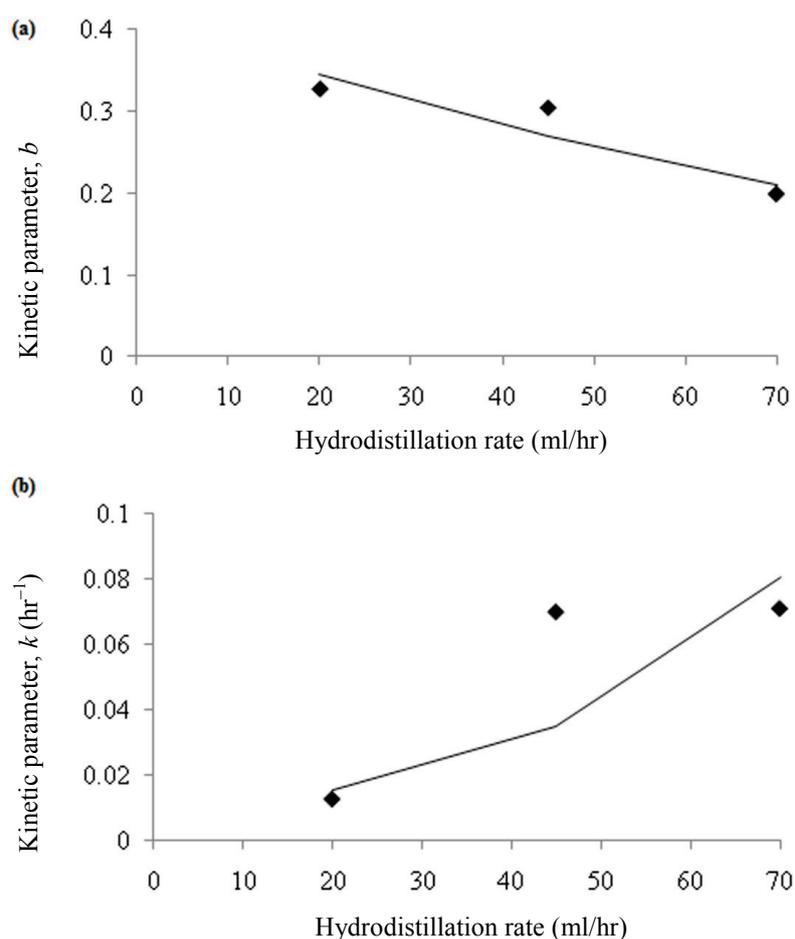


Figure 4: Validation of simulated value and experimental data of the extraction profile using Ana et al. method.

3.5.3 Hervas et al. (2006) method

Table 7 presents the extraction kinetics data obtained for the solid-liquid extraction using the Hervas et al.¹¹ method. The fit of the kinetics model proposed by Hervas et al.¹¹ yields k values of 0.144 hr^{-1} , 0.428 hr^{-1} and 1.391 hr^{-1} at hydrodistillation rates of 20 ml/hr, 45 ml/hr and 70 ml/hr, respectively. In this case, the MSE values obtained at hydrodistillation rates of 20 ml/hr and 45 ml/hr were greater than 10%, whereas for the high distillation rate (70 ml/hr), the MSE value of 2.16% was observed. This result indicated that the proposed kinetics model was suitable at higher distillation rates of the extraction process, and Figure 5 summarises the experimental behaviour of the essential oil produced in the extraction liquid.

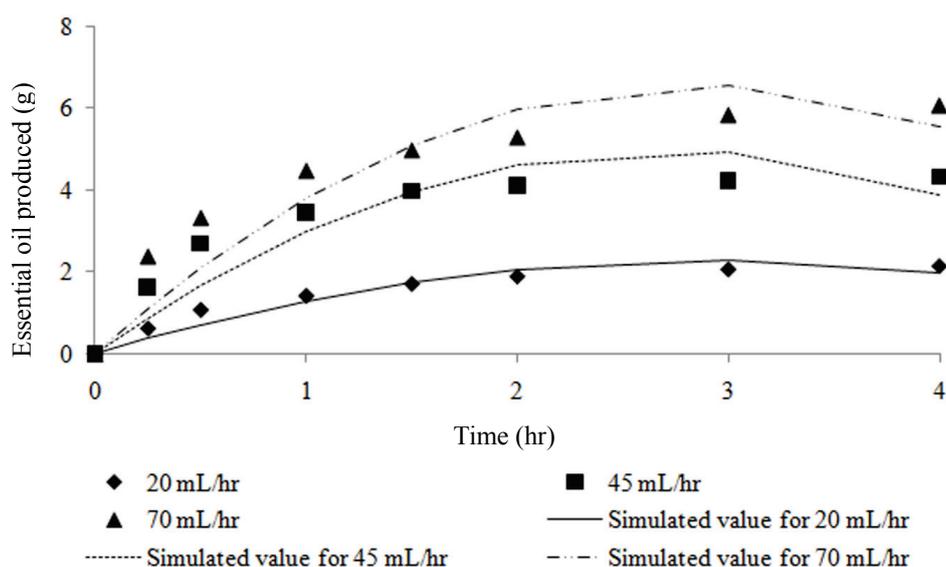


Figure 5: Validation of simulated value and experimental data of the extraction profile using Hervas et al. method.

4. CONCLUSION

Extraction of essential oil from the rhizome of *Z. cassumunar* was studied using the hydrodistillation method. Three important parameters were considered during this hydrodistillation process: time of extraction, hydrodistillation rate and solid-to-solvent ratio. The optimum parameters were then obtained using response surface methodology to obtain the maximum yield of oil of 6.64 g/g for a 4-hr extraction time, a 78-ml/hr hydrodistillation rate and a

3:150 solid-to-solvent ratio, respectively. The experimental data were found to fit well with the model described by Milojevi et al.⁸ and Ana et al.¹⁰ with MSE values lower than 10%. In this study, the mathematical model proposed by Milojevi et al.⁸ was suitable for a lower hydrodistillation rate (20 ml/hr), as the extraction process consists of two phases (i.e., fast and slow stages). The model proposed by Hervas et al.¹¹ was valid only under a high distillation rate condition (70 ml/hr). In contrast, the Ana et al.¹⁰ method could be used to describe the hydrodistillation process at all rates ranging from 20 to 70 ml/hr, showing that the extraction of essential oil from the Zingiberaceae species *Z. cassumunar* greatly depends on the hydrodistillation rate.

5. ACKNOWLEDGMENTS

The authors gratefully acknowledge the National Science Fellowship (NSF) from the Ministry of Science, Technology and Innovation (MOSTI) of Malaysia and the University Sains Malaysia for the funding provided under the Short Term research grant.

6. REFERENCES

1. Bakkali, F., Averbeck, S., Averbeck, D. & Idaomar, M. (2008). Biological effects of essential oils – A review. *Food Chem. Toxicol.*, 46, 446–475.
2. Silva, J., Abebe, W., Sousa, S. M., Duarte, V. G., Machado, M. I. L. & Matos, F. J. A. (2003). Analgesic and anti-inflammatory effects of essential oils of Eucalyptus. *J. Ethnopharmacol.*, 89, 277–283.
3. Pithayanukul, P., Tubprasert, J. & Wuthi-Udomlert, M. (2007). *In Vitro* antimicrobial activity of *Zingiber cassumunar* (Plai) oil and a 5% Plai oil gel. *Phytother. Res.*, 21, 164–169.
4. Tripathi, P., Dubey, N. K. & Shukla, A. K. (2008). Use of some essential oils as post-harvest botanical fungicides in the management of grey mould of grapes caused by *Botrytis cinerea*. *World J. Microb. Biotechnol.*, 24, 39–46.
5. Bin, J. I., Mohd, Y. M. S., Chin, C. B. & Sim, N. L. (2003). Antifungal activity of the essential oils of nine Zingiberaceae species. *Pharm. Biol.*, 41, 392–397.
6. Bhuiyan, M. N. I., Chowdhury, J. U. & Begum, J. (2008). Volatile constituents of essential oils isolated from leaf and rhizome of *Zingiber cassumunar* Roxb.. *Bangladesh J. Pharmacol.*, 3, 69–73.
7. Montgomery, D. C. (2001). *Design and analysis of experiments*, 5th ed. New York: John Wiley & Sons.

8. Milojevi, S. Z., Stojanovi, T. D., Palic, R., Lazic, M. L. & Veljkovic, V. B. (2008). Kinetics of distillation of essential oil from comminuted ripe juniper (*Juniperus communis* L.) berries. *Biochem. Eng. J.*, 39, 547–553.
9. Seader, J. D. & Henley, E. J. (2006). *Separation process principle*, 2nd ed. New York: Wiley.
10. Ana, B. K., Mirela, P., Srecko, T., Mate, B. & Darko, V. (2007). Study of solid-liquid extraction kinetics of total polyphenols from grape seeds. *J. Food Eng.*, 81, 236–242.
11. Hervas et al. (2006). Study of the extraction kinetic of glycosaminoglycans from raw sheepskin trimmings. Proceedings of International United of Environment Commission of IULTCS, Chengdu, China, 14–16 October.
12. Mat Don, M. & Shoparwe, N. F. (2010). Kinetic of hyaluronic acid production by *Streptococcus zooepidemicus* considering the effect of glucose. *Biochem. Eng. J.*, 49, 95–103.
13. Teoh, Y. P. & Mat Don, M. (2011). Kinetic model for the hydrolysis of sterilized palm press fibre. *Chem. Eng. Sci.*, 66, 3523–3530.
14. Enujiugha, V. N. & Akanbi, C. T. (2005). Compositional changes in African oil bean (*Pentaclethra macrophylla* Benth) seeds during thermal processing. *Pakistan J. Nutr.*, 4, 27–31.
15. Li, X. M., Tian, S. L., Pang, Z. C., Shi, J. Y., Feng, Z. S. & Zhang, Y. M. (2009). Extraction of *Cuminum cyminum* essential oil by combination technology of organic solvent with low boiling point and steam distillation. *Food Chem.*, 115, 1114–1119.