Vietnam Journal of Science and Technology ***56*** *(4A) (2018) 182-189*

MODELING OF ESSENTIAL OIL EXTRACTION PROCESS: APPLICATION FOR ORANGE, POMELO, AND LEMONGRASS

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Received: 17 July 2018; Accepted for publication: 6 October 2018

ABSTRACT

In this study, the kinetic models of steam distillation of orange (*Citrus sinensis (L.) Osbeck*), pomelo (*Citrus grandis L.)*, and lemongrass (*Cymbopogoncitratus*) for the recovery of essential oils were developed. The model parameters wereestimated based on experimental data and comprehensive kinetic mechanismsof the solid-liquid extraction process. Numerical results showed that, the extraction mechanism of the three materials were best fit to the Patricelli two-stage model in which the diffusion of the oil was followed by the washing step. Moreover, the model parameters obtained from the measured data reflected clearly the nature of the two-stage extraction at which the kinetic rate of the washing step (surface extraction) was higher than that of in-tissue diffusion step. Thus, the kinetics of the extraction processes obtained from the present work could be usedfor the scale-up of the extraction process operating at a large scale and for the purpose of process control as well.

Keywords: essential oil, steam distillation, modeling, optimization, kinetic.

1. INTRODUCTION

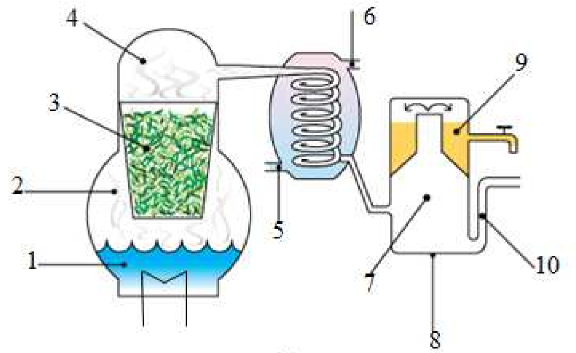
Essential oilsextracted from sweet orange (*Citrus sinensis* (L.) Osbeck), pomelo (*Citrus grandis* L.), and lemongrass (*Cymbopogoncitratus*) have useful components in the production of food, pharmacy and perfume industries [1, 2, 3]. According to literature, essential oils can be extractedby different methods, from traditional techniques to novel techniques such as solvent extraction, steam distillation, hydrodistillation, microwave extraction, ultrasound extraction and supper critical CO_2 extraction. Each method hasits own advantages and disadvantages [4, 5]. However, the steam distillation is commonly used for essential oil extraction due to safety, simplicity and environmental-friendly operations.

In order to carry out a production line at a large scale, mathematical modeling is often considered as an inventive step. Mathematical modelscan help the design, optimization and control of a processby lowering the cost of trials and experiments [6]. Thus, mathematical modeling plays an important role in the selection of process conditions. Several theoretical, empirical, and semi-empirical models were reported for the solid-liquid extraction of bioactive substances from plant materials. Most studies were developed based onthe type ofone-stage model. However this model type is not sufficient to captureall mechanisms of the extraction process due to the complicated nature of the plant oil deposition. Therefore, the objective of this work is to examine several two-stage models (washing and diffusive stage) and propose the best one that reflects well experimental data.The content of this study includes experimental conduction and kinetic modeling of essential oil steam distillation applied to sweet orange, pomelo, and lemongrass.

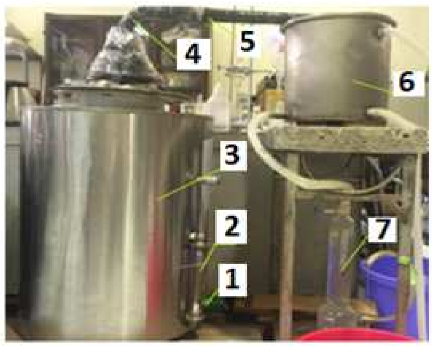
2.MATERIALS AND METHODS

2.1.Experimental lab-scale system

An experimental lab-scale system for steam distillation is shown in Figure 1. The designed capacity of the still (stripper) was10 –15 kg per batch depending on type of plants (Figure 1b). In this work, sweet orange and pomelo peels were taken from Tra Vinh province while lemongrass was brought from Quang Nam. For each run, 75 liter of purified water was initially loaded to the stripping vessel and the raw materials were chopped up to the average size of 5 – 10 mm prior to the loading step. During the extraction, the mixture of thetreated plant materials and water was heated using a 6 kW electrical resistant heater and the system was operated at atmospheric pressure. The equipment was fitted with a tight lid to prevent oil and vapor from leaking out. The system is operated in a manner that the steam rising from the still strips the oil away from the plant materials and the vapor comprised of oil and steam is passed to a condenser where the vapor phase is condensed and separated. In the decanter (the oil–water separator), the essential oil is separated from water at the top of the separator since the density of the oil is lighter than that of the remaining liquid.



(a)



(b)

Figure 1.(a) A typical diagram of a steam distillation system, (b) A photo of a lab-scale steam distillation system: (1) Water, (2) Steam Water, (3) Plant material, (4) Steam and essential oil, (5) Cold water, (6) Hot water, (7) Water and Essential oil, (8) Separator, (9) Essential oil, (10) Water.

The solid – liquid extraction was carried out for atotal of 160 minutes in which the oil recovery was measured at proper extraction time for kinetic study. Accumulated oil yield obtained from the experiments was recorded for the analysis of oil recovery. Composition of the oil obtained from the extraction of each raw material was analyzed by Gas Chromatography-Mass Spectrometry (GC-MS) on a capillary column (30 m, 0.32 mm i.d., 0.25 μm film thickness). Temperature of the column was initially set to 40 ^{o}C for 2 min, and then gradually increased to 225 ^{o}C at the rate of 4 ^{o}C/min. The extracted oil was diluted by acetone 99.99 % at the volumetric ratio of 3:100. Temperature of the injector and detector was set at 290 and 175 ^{o}C, respectively. The carrier gas (Helium gas) flow was maintained at the rate of 2.2 mL/min and the split ratio was 1:100.

2.2. Mathematical models

Kinetics modeling of solid – liquid extraction required an understanding of extraction mechanism. In the Table 1, several two-stage modeling studies have been conducted to describe extraction of different substances from various materials[7].

The extraction yield is obtained using the following equation:

$$Y(t) = \frac{Yieldofessentialoils\ at\ a\ givens\ extraction\ time}{Maximumyieldofessentialoil} \quad (1)$$

Table 1. Two-stage models for the extraction of plant materials [7].

No.	Model	Equation	Parameter
1	Parabolic Diffusion Model	$Y(t) = K_1 + K_2\sqrt{t}$(T1)	K_1 – washing kinetic coefficient K_2 – diffusive kinetic coefficient
2	Elovich Model	$Y(t) = K_1 + K_2 ln(t)$(T2)	K_1 – washing kinetic coefficient K_2 – diffusive kinetic coefficient
3	Patricelli Model	$Y(t) = A\left(1 - exp(-K_1 t)\right) + B\left(1 - exp(-K_2 t)\right)$(T3)	K_1, K_2 – kinetic coefficient for the washing and the diffusion stage A, B – final yield for washing and diffusion stage
4	So and Macdonald Model	$Y(t) = A\left(1 - exp(-K_1 t)\right) + B\left(1 - exp(-K_2 t)\right) + C\left(1 - exp(-K_3 t)\right)$(T4)	K_1, K_2, K_3 – kinetic coefficient for washing, first diffusion and second diffusion stage A, B, C – final yield for washing, first diffusion, and second diffusion stage

2.3. Statistical analyses

Mathematical modeling of the solid liquid extraction required the statistical methods of regression and correlation analysis for the model verification. The validation of models could be judgedon the basis of different statistical methods. The most widely used method in literature was root mean square error (RMSE) analysis, which was determined as follows.

$$RMSE = \sqrt{\frac{\sum_1^n (Y_i - \hat{Y}_i)^2}{n}} \quad (2)$$

The concordance between the experimental data and calculatedvalues were also examined by the coefficient of determination (R^2),

$$R^2 = 1 - \frac{\sum_{i=1}^n (Y_i - \hat{Y}_i)^2}{\sum_{i=1}^n (Y_i - \bar{Y})^2} \quad (3)$$

where Y_i – experimental value of the yield; $\hat{Y}_i$ – predicted value of the yield using the regression model; $\bar{Y}$ - arithmetic average value of the experimental yield; n – number of experimental points.

3. RESULTS AND DISCUSSION

3.1. Experimental data

Experiments of the essential oil extraction from each raw material type (sweet orange, pomelo, and lemongrass) were carried out on the lab-scale system mentioned above. For each batch experiment, the extracted oil volume with respect to extraction time was recorded so that the oil yield could be estimated as a function of processing time. Total extraction of each raw material type (sweet orange, pomelo, and lemongrass) was conducted in 150 min starting from the first liquid drop obtained at the decanter. Details of the experimental data were given in Table 2 and the description of the experimentation can be found elsewhere [5].

Table 2. Experimental data of oil recovery from the extraction of sweet orange, pomelo, and lemongrass.

Extraction Time (min)	**Sweet Orange**		**Pomelo**		**Lemongrass**	
	Extracted Oil (mL)	Oil Yield (-)	Extracted Oil (mL)	Oil Yield (-)	Extracted Oil (mL)	Oil Yield (-)
0	0	0	0	0	0	0
10	6.5	0.333	4.5	0.529	3.0	0.4
20	12	0.615	6	0.706	4.5	0.6
30	15	0.769	6.5	0.765	5.0	0.667
60	-	-	8.0	0.941	6.5	0.867
90	18.5	0.949	8.5	1.0	7.0	0.933
120	19.5	1.0	8.5	1.0	7.5	1.0
135	19.5	1.0	-	-	-	-
150	19.5	1.0	8.5	1.0	7.5	1.0

Measurement results showed that, at the first period of the extraction (about 20 min) the oil yield increased significantly with time. Then, at the second step, the extraction rate tended to decrease. According to these phenomena, it can be explained that, at the initial step, oil deposited on the surface of the raw material was washed and entrained by the steam. This step often occurred in a short time which accounted for the instant washing step. The rest part of the oil deposited in the plant's tissues was extracted at a lower rate due to the nature of the desorption mechanism. Thus, the essential oils recovered from plants can be captured well by the two-stage soli-liquid extraction.

The composition of each essential oil calculated from GC-MS analysis were given in Table 3. It can be seen that D-Limonene was the major component of the essential oils extracted from sweet orange (95.59 %) and pomelo (82.54 %) since these two materials come from the same family. Farhat *et al*. [3] also reported that the composition of Limonene in the oil extracted from orange peel by steam distillation and microwave steam distillation was around 95% and in the work of Chen *et al*. [8], Limonene concentration obtained from microwave extraction of pomelo peel was in the range of 78 – 87 %. In the case of lemongrass oil, the total content of Citral (including citronellal, citronellol, and geraniol) is around 69 % (see Table 3). Cassel *et al*. [9] reported in one of their work that, citral concentration of the lemongrass oil extracted by steam distillation is 63.5 %, while the total content of this component was in the range of 73 – 85 % in a study of Desai *et al*. [10].

Table 3. Composition of the essential oils extracted from sweet orange, pomelo, and lemongrass.

Sweet Orange			**Pomelo**			**Lemongrass**		
Compound	Content (%)	Time (min)	Compound	Content (%)	Time (min)	Compound	Content (%)	Time (min)
α-pinene, (-)-	0.51	5.27	α-Pinene	1.27	5.29	Limonene	3.295	9.685
2-β-pinene	0.10	6.38	β-Myrcene	1.50	6.69	**Citronellal**	**31.043**	**13.84**
β-Myrcene	1.65	6.64	α-Phellandrene	1.48	7.15	**Citronellol**	**10.003**	**15.92**
D-Limonene	**95.59**	**7.771**	**D-Limonene**	**82.54**	**7.79**	**Geraniol**	**27.864**	**17.06**
Octanal	0.20	30.61	γ-Terpinene	8.41	8.59			
Dibutyl phthalate	0.70	31.44	Nootkatone	1.09	28.41			

3.2. Kinetic model parameters

The four previously described models (see Table 1) were tested for the extraction ofsweet orange, pomelo, and lemongrass. Tables 4, 5, and 6 showed the corresponding results of nonlinear regression and statistical analyses for the development of the kinetic models. Numerical calculations showed that Patricelli model was the best fit for all materials (pomelo, sweet orange and lemongrass) selected in this study. It can be observed that the Patricelli model has high coefficient of determination R^2 = 0.993 and low value of RMSE (RMSE = 0.023) for pomelo; R^2 = 0.997 and RMSE = 0.017 for sweet orange; and R^2 = 0.999, RMSE = 0.011 for lemongrass.

Table 4. Coefficients and statistical parameters of extraction modeling for sweet orange.

Model	**Coefficients**						**RMSE**	**R^2**
	K_1	K_2	K_3	A	B	C		
Parabolic Diffusion	0.287	0.064	-	-	-	-	0.072	0.946
Elovich	0	0.204	-	-	-	-	0.051	0.973
Patricelli	**0.048**	**0.0002**	**-**	**0.964**	**1.089**	**-**	**0.017**	**0.997**
So and Macdonald	0.0001	0.048	0	0.871	0.964	1.968	0.018	0.997

Table 5. Coefficients and statistical parameters of extraction modeling for pomelo.

Model	**Coefficients**						**RMSE**	**R^2**
	K_1	K_2	K_3	A	B	C		
Parabolic Diffusion	0.525	0.043	-	-	-	-	0.056	0.962
Elovich	0.187	0.170	-	-	-	-	0.031	0.988
Patricelli	**0.131**	**0.014**	**-**	**0.648**	**0.424**	**-**	**0.023**	**0.993**
So and Macdonald	0.107	0.0005	0	0.870	1.974	4.984	0.048	0.972

Table 6. Coefficients and statistical parameters of extraction modeling for lemongrass.

Model	**Coefficients**						RMSE	R^2
	K_1	K_2	K_3	A	B	C		
Parabolic Diffusion	0.286	0.064	-	-	-	-	0.048	0.972
Elovich	0	0.203	-	-	-	-	0.028	0.990
Patricelli	**0.140**	**0.023**	**-**	**0.359**	**0.671**	**-**	**0.011**	**0.999**
So and Macdonald	0.995	0.039	0.001	0.173	0.705	0.714	0.014	0.998

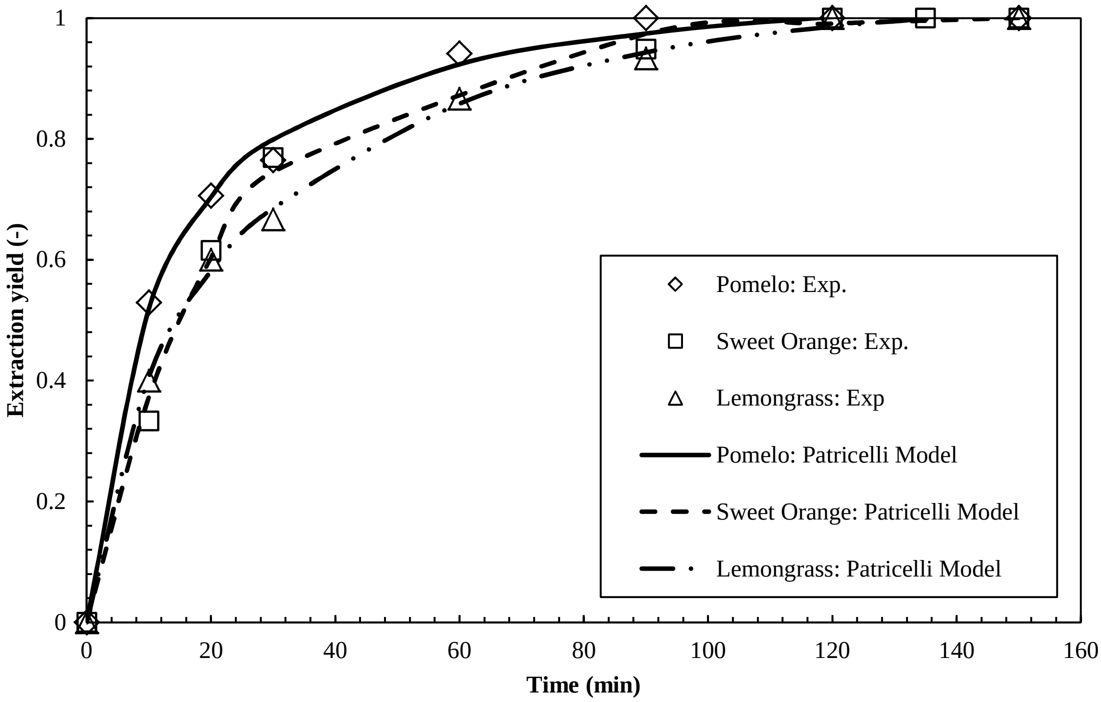


Figure 2. Extraction kinetics of pomelo, sweet orange, and lemongrass.

Experimental data of the oil yield obtained from experiments were depicted in comparison with predicted model in Figure 2. It can be seen that, the Patricelli model captured well the two-stage extraction mechanism of theoil deposition in the plants. For the extraction of pomelo and sweet orange, the washing stage was more important than diffusion stage. This may be explained that the amount of essential oil located on the surface of the skin was higher than the oil deposited inside the plant tissues. For instance, the oil deposited on the skin surface of sweet orange peels occupied more than 96 % of the total oil yield (see Table 2). However, due to the fiber structure of lemongrass, the amount of in-cell oil (67.1 %) was higher than the oil deposited on the cell surface (35.9 %).In addition, numerical results given in Table 2 also showed that the extraction rate of the surface oil was higher than that of in-tissue oil since the values of K_1 were always higher than that of K_2 for all selected materials (sweet orange, pomelo, and lemongrass).

Details of kinetic models for the extraction of selected materials in this work were described in Equations (4), (5), and (6) as follows.

For sweet orange:

$$Y(t) = 0.964\big(1 - exp(-0.048t)\big) + 1.089\big(1 - exp(-0.0002t)\big) \tag{4}$$

For pomelo:

$$Y(t) = 0.648\big(1 - exp(-0.131t)\big) + 0.424\big(1 - exp(-0.014t)\big) \tag{5}$$

For lemongrass:

$$Y(t) = 0.359\big(1 - exp(-0.139t)\big) + 0.671\big(1 - exp(-0.023t)\big) \tag{6}$$

4. CONCLUSIONS

Kinetics of theessential oil extraction from different plants (sweet orange, pomelo, and lemongrass) using steam distillation were developed on the basis of semi-theoretical models. The results showed that all models selected are in a good agreement with experimental data. Howerver, the Patriicelli model, in which both washing and desorption steps were accounted for, can capture wellthe extraction kinetics of all materials (sweet orange, pomelo, and lemongrass) considered in the present work. The proposed mathematical models can be useful for the process design of large scale systems and for the purpose of process control.

Acknowledgements. This work is funded by the Hanoi University of Science and Technology (HUST) under project T2017-PC-020.

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