YIELD ANALYSIS OF ESSENTIAL OILS EXTRACTED BY STEAM DISTILLATION

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Abstract: A comparative analysis of models describing the change in yield of essential oil over time is presented in the article. Nonlinear models, third-order polynomial and second exponential model describe with sufficient precision the change of experimental data over time. These models can be used to predict the extraction time of essential oils. The results can be useful in planning and managing the production of essential oils. For this purpose, further research is needed to determine the diffusion coefficient and to analyze the impact of the individual elements of the process on the production of essential oils.

Keywords: Essential oil, Steam distillation, Mathematical model, Rosemary, Basil, Lavender, Citronella, Dill, White oregano.

1. INTRODUCTION

Essential oils are used in pharmaceuticals, food and fodder production, perfumery. They are obtained by the extraction of volatile chemicals contained in most plants. Different methods are used to extract essential oils depending on the nature of the plant material and the desired properties of the product, such as distillation with water and water vapor, extraction with volatile solvents, entrainment, maceration and compression. Distillation is often used because it is simplified, convenient, with low cost of equipment working method.

According to the classification presented in the available literature [1,5], the models of the extraction process of essential oils can be divided into three categories: empirical models, liquid phase based mass balance models and solid-based models phase of the mass balance.

Various modeling strategies are used in practice, given the characteristic to be analyzed in the extraction process of essential oil. This model, which takes into account the plant's specificity in the extraction process of essential oil, is suitable [2].

The purpose of this article is to analyze mathematical models based on a solid phase of the mass balance to predict the yield of essential oil.

2. MATERIAL AND METHODS

2.1. Model of extraction process of essential oils

The extraction model was prepared according to the method presented in [3,4] and supplemented by [10]. The extraction process is diffuse. This process can be approximated by a model based on Fick's law as established and one-dimensional, by rectangular geometry. It can be assumed that the solution of plant material and water is homogeneous and consistent in composition. In the boundary areas of the vessel the evaporating water carries a small amount of essential oil and its concentration of C_A branches to 0 ($C_A=0$). D is the diffusion coefficient. The described here may be presented as a second-order differential equation. The left part is a second derivative of x , and in the right part is the first derivative of time t :

$$\frac{\partial^2 C_A}{\partial x^2} = \frac{1}{D} \frac{\partial C_A}{\partial t}, \text{ in } 0 \leq x \leq L \quad (1)$$

The initial state of the concentration at time $t=0$ is:

$$C_A = C_{A_0} \text{ in } t = 0 \quad (2)$$

The boundary conditions for the concentration are:

$$\begin{aligned} C_A &= 0 \text{ in } x = 0 \\ C_A &= 0 \text{ in } x = L \end{aligned} \quad (3)$$

indicating that the concentration is zero in the evaporating vapor around the walls of the vessel in which the aqueous extraction takes place.

In the case L is the wall thickness of the vessel and D is the effective diffusion coefficient.

The above equations are a solution to the Sturm-Liouville problem, which uses a technique for separating variables [8]. The function of the essential oil concentration relative to x and the time t , can be expressed as:

$$C_A(x, t) = \sum_{n=1}^{\infty} \frac{4C_{A_0}}{n\pi} \text{sen}(\beta_n x) e^{-D\beta_n^2 t} \quad (4)$$

where:

$$\beta_n = \frac{n\pi}{L}, n = 1, 2, 3 \dots \infty \quad (5)$$

sen is referred to as a trigonometric function corresponding to a sinusoidal one. The mark from the original methodology of the mentioned authors is used.

The mass flow as a function of time is derived from the mass flow at the boundary multiplied by the result of the normal surface [10]:

$$\dot{m}_A(t) = \frac{4C_{A_0}DA}{L} \sum_{n=1}^{\infty} e^{-D\beta_n^2 t} \quad (6)$$

The extracted mass of the soluble elements of the plant composition is:

$$m_A(t) = \frac{8m_{A_0}}{\pi^2} \sum_{m=0}^{\infty} \frac{\left(1 - e^{-\frac{(2m+1)^2 \pi^2 Dt}{L^2}}\right)}{(2m+1)^2} \quad (7)$$

The extraction rate can be determined by:

$$e(t) = \frac{m_A(t)}{m_A(\infty)} = \frac{\sum_{m=0}^{\infty} \frac{\left(1 - e^{-\frac{(2m+1)^2 \pi^2 Dt}{L^2}}\right)}{(2m+1)^2}}{\sum_{m=0}^{\infty} \frac{1}{(2m+1)^2}} \quad (8)$$

2.2. Mathematical models

The GNU Octave software has been used. The models are obtained with *fit(x, y, 'type')* function, where x and y are input data, and type is the type of model. Table 1 presents the models used in the present work that are used to describe the change in time of essential oil data. Their choice is based on the more commonly used models in the available literature to describe such processes [9,11].

Table 1. Models used to describe extraction processes

Model name	First-order polynomial	Second-order polynomial	Third order polynomial	First exponential	Second exponential
Designation in software	poly1	poly2	poly3	exp1	exp2
Linear form	$y=a*x + b$	$y=a*x^2 + b*x + c$	$y=a*x^3 + b*x^2 + c*x + d$	$y=a*\exp(b*x)$	$y=a*\exp(b*x) + c*\exp(d*x)$
Formula $y=f(t)$	$y(t) = at + b$	$y(t) = at^2 + bt + c$	$y(t) = at^3 + bt^2 + ct + d$	$y(t) = ae^{bt}$	$y(t) = ae^{bt} + ce^{dt}$

Table 2. Parameters for estimating the average model versus experimental data

Parameter	Formula	Description
Regression coefficient R^2	$R^2 = \frac{r_{ss}}{t_{ss}}$ $t_{ss} = \sum_{i=1}^n (y_i - y_{mean})^2$ $r_{ss} = \sum_{i=1}^n (y_i - y_{i\ fit})^2$	y_i – measured values y_{mean} – average of measured values y_{fit} – values of the model n – number of measurements
Sum of squared errors SSE	$SSE = \frac{1}{n} \sum_{i=1}^n (y_{i\ pred} - y_i)^2$	$y_{i\ pred}$ – predicted values y_i – measured values n – number of measurements
Root mean squared error RMSE	$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_{i\ pred} - y_i)^2}$	n – number of measurements
Mean square error MSE	$MSE = \frac{\ y - y_{model}\ ^2}{N_s}$	N_s – number of samples; $\ $ - normed vector
Normed root mean squared error NRMSE	$NRMSE = 1 - \frac{\ y_{model}(:, i) - y(:, i)\ }{\ y_{model}(:, i) - mean(y_{model}(:, i))\ ^2}$	$i=1 \dots n$ – number of measurements NRMSE is changed by inf - the model does not describe the data; 1 - the model describes the data with sufficient precision
Normed mean squared error NMSE	$NMSE = 1 - \frac{\ y_{model}(:, i) - y(:, i)\ ^2}{\ y_{model}(:, i) - mean(y_{model}(:, i))\ ^2}$	NMSE is changed by inf - the model does not describe the data; 1 - the model describes the data with sufficient precision

2.3. Model accuracy evaluation

The GNU Octave software has been used. The ability to describe the experimental data with those of its model is done with the *goodnessOfFit* function *goodnessOfFit(y, ymodel, 'type of error')* where *y* is the experimental data, *ymodel* are the points of the model, *type of error* is the type of error, which assesses the model [7]. This function calculates a mean square error, a normalized root of a normal error, a normalized error.

In this analysis different data for essential oils is used that have not been involved in compiling the averaged models. Table 2 describes the parameters used to analyze an average model.

Data on essential oils from white oregano and dill plants was provided by the Department of Food Technology at the Faculty of Engineering and Technology in Yambol, Bulgaria [1,6]. Oils are obtained by aqueous extraction using a ratio of 1/10 material to water. Three samples of each type of essential oil were used, the results for which were averaged.

The data obtained are compared with those for rosemary, basil, lavender, citronella, presented in [3,4].

The extraction rate *e*, g/g according to the extraction process of essential oils is determined by the mathematical dependencies presented. Table 3 gives results for six plants.

Table 3. Change of extraction rate (*e*, g/g) for essential oils from six plants

t, min	Rosemary <i>e</i> , g/g	Basil <i>e</i> , g/g	Lavender <i>e</i> , g/g	Citronella <i>e</i> , g/g	Dill <i>e</i> , g/g	White oregano <i>e</i> , g/g
0	0,000	0,000	0,000	0,000	0,000	0,000
10	0,810	0,720	0,490	0,333	0,111	0,338
20	0,960	0,980	0,840	0,583	0,481	0,549
30	0,960	0,980	0,910	0,667	0,704	0,775
40	0,960	0,980	0,910	0,750	0,926	0,901
50	0,960	0,980	0,910	0,750	1,000	0,958
60	0,960	0,980	0,910	0,792	1,000	1,000
70	0,960	0,980	0,910	0,833	1,000	1,000
80	0,960	0,980	0,910	0,917	1,000	1,000

3. RESULTS AND DISCUSSION

For the first four plants - rosemary, basil, lavender and citronella, data from literature sources were used, and data from the Department of Food Technologies was used for white oregano and dill. The extraction rate is set for 20 minutes for rosemary and basil. In lavender, this process is slower than the other two and has a lower extraction rate. The citronella process was not detected for the period of 80 minutes and the extraction rate slowly increased. Compared to the data on rosemary, basil, lavender and citronella, the degree of extraction for dill is found for 50 minutes, whereas for white oregano this index is set for 60 minutes.

An analysis of the yield of essential oils from the six plants under consideration was made. Figure 1 shows results for the variation of this indicator from four different plants compared to the data on dill and white oregano.

a) rosemary, basil, lavender and citronella according to [3,4]

b) white oregano and dill

Figure 1. Processes of changes in the yield of essential oils

Table 4. Results of model analysis

	Rosemary					Basil					Lavender				
	poly1	poly2	poly3	exp1	exp2	poly1	poly2	poly3	exp1	exp2	poly1	poly2	poly3	exp1	exp2
a	0,000	0,000	0,000	0,019	0,027	0,000	0,000	0,000	0,012	0,018	0,000	0,000	0,000	0,014	0,029
b	0,017	0,001	0,000	0,007	0,001	0,011	0,001	0,000	0,008	0,002	0,012	0,001	0,000	0,009	-0,002
c	NaN	0,008	0,002	NaN	-0,027	NaN	0,005	0,001	NaN	-0,018	NaN	0,004	0,002	NaN	-0,029
d	NaN	NaN	0,003	NaN	-1,156	NaN	NaN	0,001	NaN	-1,133	NaN	NaN	0,000	NaN	-0,079
SSE	0,000	0,000	0,000	0,001	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
R ²	0,371	0,717	0,913	0,313	0,987	0,423	0,782	0,953	0,355	0,958	0,531	0,885	0,989	0,439	0,993
dfe	7,000	6,000	5,000	7,000	5,000	7,000	6,000	5,000	7,000	5,000	7,000	6,000	5,000	7,000	5,000
R ² adj	0,281	0,622	0,861	0,215	0,979	0,341	0,710	0,924	0,262	0,933	0,464	0,847	0,983	0,359	0,989
RMSE	0,008	0,006	0,004	0,008	0,001	0,005	0,004	0,002	0,006	0,002	0,006	0,003	0,001	0,007	0,001
MSE	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
NMSE	-0,695	0,605	0,905	-1,565	0,987	-0,364	0,722	0,950	-1,137	0,956	0,115	0,870	0,989	-0,554	0,993
NRMSE	-0,302	0,372	0,691	-0,601	0,886	-0,168	0,472	0,777	-0,462	0,791	0,059	0,639	0,897	-0,247	0,918
	Citronella					Dill					White oregano				
	poly1	poly2	poly3	exp1	exp2	poly1	poly2	poly3	exp1	exp2	poly1	poly2	poly3	exp1	exp2
a	0,000	0,000	0,000	0,009	0,015	0,000	0,000	0,000	0,009	0,750	0,001	0,000	0,000	0,019	4,965
b	0,006	0,001	0,000	0,014	0,005	0,004	0,001	0,000	0,016	-0,012	0,012	0,001	0,000	0,013	-0,014
c	NaN	0,002	0,001	NaN	-0,015	NaN	-0,002	0,001	NaN	-0,752	NaN	0,001	0,002	NaN	-4,965
d	NaN	NaN	0,001	NaN	-0,069	NaN	NaN	-0,002	NaN	-0,014	NaN	NaN	0,000	NaN	-0,015
SSE	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,001	0,000
R ²	0,860	0,971	0,990	0,746	0,994	0,824	0,978	0,980	0,673	0,968	0,807	0,994	0,998	0,674	0,997
dfe	7,000	6,000	5,000	7,000	5,000	7,000	6,000	5,000	7,000	5,000	7,000	6,000	5,000	7,000	5,000
R ² adj	0,840	0,961	0,984	0,710	0,990	0,799	0,971	0,969	0,626	0,949	0,780	0,992	0,997	0,628	0,996
RMSE	0,003	0,001	0,001	0,004	0,001	0,005	0,002	0,002	0,007	0,002	0,008	0,002	0,001	0,010	0,001
MSE	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
NMSE	0,837	0,970	0,990	0,600	0,994	0,786	0,978	0,980	0,396	0,967	0,761	0,994	0,998	0,415	0,997
NRMSE	0,596	0,827	0,899	0,368	0,921	0,537	0,851	0,859	0,223	0,818	0,512	0,921	0,955	0,235	0,950

The results of the analysis of five mathematical models describing the changes of the yield of essential oils are presented in Table 4. From this table it can be seen that the data for rosemary can be described with sufficient accuracy by a second exponential model. The yield of basil essential oil is described by third order polynomial and second exponential models. A similar result is obtained for lavender. Citronella, dill and white oregano data can be described except for both models and second order polynomial. From a practical point of view, it is good to choose a model other than a polynomial, because in some cases the model can begin to oscillate around the experimental data, resulting in unrealistic results - for example negative yields.

4. CONCLUSION

A comparative analysis of models describing the change in yield over time has been made. Nonlinear models third-order polynomial and second exponential model describe with sufficient precision the change of experimental data over time.

The models obtained can be used to predict the extraction time of essential oils. The results can be useful in planning and managing the production of essential oils. For this purpose, further research is needed to determine the diffusion coefficient and to analyze the impact of the individual elements of the process on the production of essential oils.

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