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Kinetic parameters for the distillation process in obtaining essential oil from fennel fruits

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Abstract. A steam experimental distillation process was investigated to extract essential oil from fennel fruits in a laboratory installation. The chemical composition of the extracted primary essential oil was investigated. Based on performed experiments, the kinetic parameters at three different temperatures of the supplied steam (these are the molecular internal diffusion coefficient, activation energy, effective diffusion coefficient, process speed, and rate constant) were calculated. The obtained results showed that the most suitable temperature for the supplied superheated steam during the distillation of the essential oil from fennel fruits is 150 °C. At this temperature, it is possible to reduce the duration of the process and extract the maximum essential oil from the raw material.

1 Introduction

Plant species are diverse and contain a number of volatile components. These components can be extracted by various methods. The most commonly used are distillation, volatile solvent extraction, subcritical carbon dioxide extraction, and various microwave extractions [1].

Fennel (Foeniculum vulgare Mill.) is a species from central Europe and the Mediterranean area, and is one of the most widely spread plants used in the medical industry. The fennel is grown extensively in arid and semi-arid regions, and according to [2] is one of the oldest spice plants. Fennel has pronounced medicinal properties and is used for gastrointestinal and neurological disorders, vomiting, kidney stones, and diarrhea; furthermore, it has antiseptic, antispasmodic, antiulcer, and carminative properties [3]. Nowadays, much attention is paid to fennel due to its seeds' health and nutritional value, which are rich in volatile and vegetable oils [3]. Fennel seeds are known to have many health-beneficial elements, such as vitamins and minerals, which is the reason for their application in the perfumery, cosmetic, pharmaceutical, and food industries [4].

Furthermore, the seeds of the fennel plant can be used to obtain high-quality essential or vegetable oils, and the remaining parts (leaves, stems, and roots) can find various applications as a spice in cooking, perfumery, and pharmacy according to [2].

The main methods for obtaining essential oil from plant raw materials are: distillation, extraction, absorption, and mechanical extraction [1].

The distillation process from essential oil raw materials can be through steam, water, or steam distillation [1].

This article examines the steam distillation of ground fennel fruits to calculate the kinetic parameters of the process at three different temperatures. The determined kinetic parameters include the molecular internal diffusion, activation energy, rate constant, effective diffusion coefficient, and process rate.

According to [5], the mass transfer, related to the extraction of essential oils, is represented by two phases: diffusion of the essential oil from the interior of the cells to the surface and mass transfer from the surface to the solvent. Furthermore, this model assumes the occurrence of two simultaneous processes: (a) rapid distillation of the essential oil from the external surfaces of plant particles (also known as flushing); and (b) slow diffusion of the essential oil through the plant particles [6].

An expression of the diffusion properties when extracting components from plant material is the molecular diffusion coefficient [6]. It assumes individual values for different plants and plant organs.

According to some authors [7-10], the influence of temperature is mainly on the process of extracting the essential oil, expressed through the Arrhenius law, where the reaction rate constant (k) is determined. On this basis, graphical relationships between lnk and the process temperature 1/T can be made, and the activation energy of the system, entropy, and enthalpy can be determined. The effective diffusion coefficient can be estimated using Arrhenius' law, establishing a relationship between the kinetic parameters (activation energy and internal molecular diffusion coefficient) and thermodynamic parameters (Gibbs energy, enthalpy, entropy, and temperature) of the process. The estimated reaction rate constant for a certain thermodynamic system allows obtaining information about the order, rate, and mechanism of the reaction, which can be used to optimize the process [10].

The literature provides values of diffusion coefficient: for sage leaves it is $16.61.10^{-9}$ $m^2.s^{-1}$ [11], for hawthorn leaves - $9.82\text{-}548.10^{-9}$ $cm^2.s^{-1}$ [12], and for paulownia leaves - $68.9.10^{-12}$ $cm^2.s^{-1}$ [10]. The diffusion coefficient results are related to the nature of the raw material (cellular structure, porosity, size, etc.), the available bioactive substances, and the conditions of the extraction process, as well as the solvent and temperature [10].

In the literature [10], data on the parameters of the extraction process of caraway seeds are presented. The Gibbs free energy (up to 2549.46 to 7090.88 $kJ.mol^{-1}$), entropy (up to -86.62 to 16.87 $kJ.mol^{-1}.K^{-1}$) and enthalpy (up to -1739.49 to 27778.19 $kJ.mol^{-1}$) of the process were determined, as well as the kinetic parameters: activation energy (up to 1739.49 to 27778.19 $kJ.mol^{-1}$), effective diffusion coefficient (up to 2.40 to $111.31.10^{-3} m^2 s^{-1}$) and reaction rate constant (up to 0.61 to $3.36.10^{-3} s^{-1}$) of the process.

2 Material and methods

The activation energy (E_a) of the process was determined according to equation (1) given in Ref. [10]:

$$E_a = 2.3R.T.tg\alpha \tag{1}$$

According to the Beloborodov equation (2), the molecular diffusion coefficient can be calculated by applying the procedure described in [10-12] for extracting essential oil from fruits.

$$D = \frac{l^2 2.3lg(E_1 - E_2)}{\pi^2.(\tau_1 - \tau_2)} \tag{2}$$

where: l is the size of the material, cm; τ_1, τ_2 – the duration of the process, s; E_1, E_2 – the initial and the final concentration of essential oil, % [10].

The diffusion properties of the extracted substance, as well as the running of the process, are strongly affected by the temperature. Its influence can be expressed by the reaction rate constant using the following equation [10]:

$$k = A.e^{-\frac{E_a}{RT}} \tag{3}$$

where: k is the reaction rate constant, Ea is the activation energy in J/mol, R is the universal gas constant in J/mol·K, and T is the absolute temperature in K.

Using the Arrhenius law, the effective diffusion coefficient (De) was determined, which varies depending on temperature and gives the relationship between the kinetic and thermodynamic parameters of the process described in [7, 8].

And to obtain the effective diffusion coefficient De in $m^2.s^{-1}$, the following equation can be used [7, 8]:

$$D_e = D_o.e^{\frac{E_a}{R.T}} \tag{4}$$

where D_o is either the pre-exponential factor or the internal molecular diffusion coefficient in $m^2.s^{-1}$.

3 Results and Discussion

The chemical composition of the primary essential oil was determined as explained in [13]. Fig. 1 shows the graphical dependence of the extracted essential oil over the duration of the process.

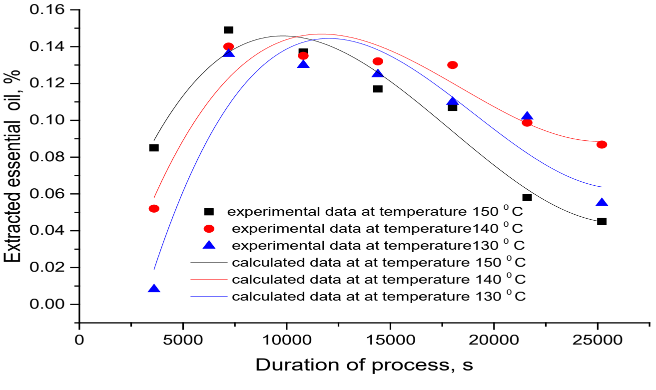

Fig.1. Content of essential oil during the process

It can be seen from the graphical dependence that the highest % of essential oil is extracted when steam is supplied at a temperature of 140 °C. But the most successful is the process occurring at a steam temperature of 150 °C.

As a process, diffusion is influenced by a number of factors, such as the particle surface area, particle size, and temperature [13]. According to [7], better diffusion is achieved for higher extraction temperatures. In source [1], the diffusion coefficients for the extraction of essential oils from rosemary, basil, and lavender were obtained to be $4.36.10^{-11}$, $5.96.10^{-11}$, and $3.32.10^{-11}$ m²/s, respectively. In Ref. [5], from mace essential oil extracted by hydro distillation, the value of the coefficient of diffusion is $4.98.10^{-14}$ m^2/s, and by microwaveassisted hydro distillation at different powers (300/600/800 W), the coefficient is $9.17.10^{-14}/1.39.10^{-13}/1.65.10^{-13}$ m^2/s, respectively.

In this paper, the kinetic parameters for a distillation process at three different temperatures of the superheated steam feed have been calculated. The data from the calculations are presented in Tables 1 to 3.

Table 1. Kinetic parameters at a temperature of 130 °C

τ, s	**$D.10^{-6}$, $m^2.s^{-1}$**	**$De.10^{-9}$ $m^2.s^{-1}$**	**$k.10^{-15}$, s^{-1}**	**$r.10^6$, $mol.m^{-3}.s^{-1}$**
3600	0.39	38.70	10.83	1.73
7200	0.25	24.59	199.22	16.85
10800	0.26	25.29	189.48	10.65
14400	0.26	25.87	181.43	7.63
18000	0.28	27.58	157.68	5.27
21600	0.29	28.49	145.25	4.03
25200	0.34	33.70	75.40	1.76

Table 2. Kinetic parameters at a temperature of 140 °C

τ, s	**$D.10^{-6}$, $m^2.s^{-1}$**	**$De.10^{-9}$, $m^2.s^{-1}$**	**$k.10^{-15}$, s^{-1}**	**$r.10^6$, $mol.m^{-3}.s^{-1}$**
3600	0.34	34.02	2.66	11.58
7200	0.24	24.13	7.68	17.44
10800	0.25	24.71	7.38	11.14
14400	0.25	25.06	7.20	8.13
18000	0.26	25.29	7.08	6.39
21600	0.29	28.86	5.23	3.88
25200	0.30	30.20	4.56	2.88

Table 3. Kinetic parameters at a temperature of 150 °C

τ, s	$D.10^{-6}$, $m^2.s^{-1}$	$De.10^{-9}$, $m^2.s^{-1}$	$k.10^{-15}$, s^{-1}	$r.10^{6}$, $mol.m^{-3}.s^{-1}$
3600	0.33	33.04	3.21	13.73
7200	0.23	23.08	8.44	18.79
10800	0.25	24.48	7.68	11.33
14400	0.27	26.78	6.45	7.07
18000	0.28	27.92	5.85	5.10
21600	0.34	33.37	3.05	2.17
25200	0.35	34.78	2.34	1.42

From the values obtained for the kinetic dependencies, the following can be concluded: in the process of distillation with superheated steam, the most suitable temperature is 150 °C. The diffusion coefficient for all three temperatures initially has high values, which decrease and then increase again. This can be explained as follows: at first, the oil is extracted on the surface of the raw material, and later in depth.

The obtained values for the diffusion coefficient confirm the claims of the authors of Ref. [6] that the process of extracting the essential oil goes through two phases. The first phase is the extraction of the essential oil from the surface of the raw material, and the second phase is from the interior of the raw material.

According to the authors of the literature [5], a higher diffusion coefficient guarantees faster extraction of the essential oil. According to the literature [7], a higher temperature is a prerequisite for better extraction of the essential oil.

The values for the rate constant of the process are lowest for a steam supply temperature of 150 °C, which means the reaction is stable and proceeds slowly. The calculated values for the reaction rate are lowest at a temperature of 150 °C.

The activation energy required to carry out the process at different temperatures of the supplied steam has also been calculated. For a feed steam temperature of 130 °C, the activation energy value is -7742.63 $J.mol^{-1}$, at a temperature of 140 °C, the activation energy is -7934.69 $J.mol^{-1}$, and at 150 °C, it is -8126.74 $J.mol^{-1}$. The negative sign of the activation energy means that in order to carry out the process, an input of energy is required, which increases with the increase in the temperature of the feed superheated steam.

In Ref. [14,15] are given the values of the coefficient of diffusion for different temperatures: at 50 ^0C it is $1.07.10^{-12}$ $m^2.s^{-1}$; at 70 ^0C - $1.74.10^{-12}$ $m^2.s^{-1}$; at 80 ^0C - $2.06.10^{-12}$ $m^2.s^{-1}$, and at 90 ^0C - $3.02.10^{-12}$ $m^2.s^{-1}$ obtained by extraction of polysaccharide from *Spirullina*.

4 Conclusion

The kinetic parameters (molecular internal diffusion coefficient, activation energy, effective diffusion coefficient, process speed, and rate constant) were calculated at three different temperatures of the supplied steam for a process of distillation, and an essential oil from fennel fruits was obtained. The obtained results allow us to conclude that the most suitable temperature of the supplied superheated steam during distillation is 150 °C. At this temperature, it is possible to reduce the duration of the process and extract the maximum essential oil from the raw material. Another result from the carried out experiments is the calculated kinetic parameters of fennel essential oil. The estimated values correspond to those obtained in previous studies.

References

[1] E. Cassel, R.M.F. Vargas, N. Martinez, D. Lorenzo, E. Dellacass, Steam distillation modeling for essential oil extraction process, Industrial Crops and Products, **29**, 171–176, (2008). https://doi.org/10.1016/j.indcrop.2008.04.017

[2] L. Barros, A.M. Carvalho, I.C.F.R. Ferreira, The nutritional composition of fennel (Foeniculum vulgare): shoots, leaves, stems and inflorescences, LWT Food Sci. Technol. **43**, 814–818 (2010). http://dx.doi.org/10.1016/j.lwt.2010.01.010

[3] M. Ghanem, H. Radwan, E. Mahdy, Phenolic compounds from Foeniculum vulgare (Subsp: Piperitum)(Apiaceae) herb and evaluation of hepatoprotective antioxidant activity, Pharmacognosy, **4**, 104–108 (2012). https://doi.org/10.4103/0974-8490.94735

[4] M.I. Nassar, E.A. Aboutabl, Y.A. Makled, E.-D.A. El-Khrisy, A.F. Osman, Secondary metabolites and pharmacology of Foeniculum vulgare Mill. Subsp. Piperitum, Rev. Latinoam. química **38**, 103–112 (2010).

[5] D.S. Fardhyanti, W.B. Sediawan, A. Hisyam, Kinetics of mace (Myristicae arillus) essential oil extraction using microwaveassisted hydrodistillation: Effect of microwave power, Ind. Crops&Prod., **131**, 315-322 (2019). https://doi.org/10.1016/j.indcrop.2019.01.067

[6] V. Kafarov, Basics of Mass Transfer (Visshaya Shkola, Moscow, 1962).

[7] A. Tusek, M. Benkovic, A. Cvitanovic, D. Valinger, T. Jurina and J. Kljusuric, Industrial Crops and Products, **91**, 205-214 (2016).

[8] C.F. Uzoh, O.D. Onukwuli, J.T. Nwabanne, Characterization, kinetics and statistical screening analysis of gmelina seed oil extraction process. Mater Renew Sustain Energy **3**, 38 (2014).

[9] J. Nwabanne, International Journal of Multidisciplinary and Engineering, **3**, 6, 11 (2012).

[10] S. Tasheva, Mass-Transfer Processes by Cohobation of Distillation Waters and Extraction of Essential Oils in Raw Material, DSc Thesis, UFT, Plovdiv (2014) (in Bulgarian).

[11] S. Mollova, Technological studies on extracts from garden tea (Salvia officinalis L.), PhD Thesis, UFT, Plovdiv (2017) (in Bulgarian).

[12] M. Ergezen, Technology for obtaining of the aromatic products from plants from genus Crataegus, PhD Thesis, UFT, Plovdiv (2014) (in Bulgarian).

[13] A. Semerdhzieva, D. Atanasov, T. Atanasova, S. Tasheva, Thermodynamic parameters for distillation process in obtaining essential oil from cut fruits, 10th International Conference on Energy Efficiency and Agricultural Engineering (EE&AE), 5-7 November 2025 (2025) (in press).

[14] R. Ruiz, C. Martinez, M. Vizcarra, Modeling conventional and ultrasound-assisted extraction of oil-containing materials, Revista Mexicana de Ingenieria Quimica **10**, 3, 387-399 (2011).

[15] R. Chaiklahan, N. Chirasuwan, P. Triratana, S. Tia, B. Bunnag, Effect of extraction temperature on the diffusion coefficient of polysaccharides from *Spirulina* and the optimal separation method, Biotechnol. Bioprocess Eng. **19**, 369–377 (2014).