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Thermodynamic parameters for the distillation process in obtaining essential oil from cut fruits

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Abstract. An experimental steam distillation process was investigated to extract essential oil from cut fruits in a laboratory distillation plant. It was determined that the chemical composition of the obtained primary essential oil. The experiments were performed at three different temperatures of the supplied steam. The thermodynamic parameters (Gibbs energy, enthalpy, and entropy) were calculated. The pressure drop in the distillation apparatus was also measured when the steam was passing through the layer of ground raw material.

1 Introduction

The essential oils (EOs) are products obtained from different parts of plants, such as leaves, flowers, stems, roots, and barks, or from the aboveground part of plants [1-3]. In the most general case, essential oils are multi-component mixtures [2-3]. Chemically, essential oils are homogeneous mixtures made up of many components, composed of a number of fractions, from the most volatile to the heaviest terpenoids, which, according to [4], are natural compounds in most cases produced as secondary metabolites and acting as protective phytochemicals for plants. Terpenoids have a pronounced aroma, which in most cases is pleasing to the human sense of smell. Furthermore, according to [2-4], its density is usually lower than that of water; each species is characterized by its color with varying intensity. Due to these and other characteristics, as well as their wide range of applications, essential oils are in great demand. The aromatic, flavoring, and pharmaceutical properties of essential oils play a major role in various industrial sectors, for example, in supplying raw materials for the perfume and cosmetic industries, the pharmaceutical industry, aromatherapy, food, and canning industries [2, 4]. According to [5], the mass production of essential oils (EOs) is a driving force in the global market; however, high market prices are often a major obstacle to market. Furthermore, the high demand for essential oils is of particular importance, as natural preservatives, providing growth opportunities in the global market [5].

Fennel (Foeniculum vulgare Mill.) is from the *Apiaceae* family. It may be a wild or cultivated, aromatic, perennial herbaceous plant, which is characterized by a small, light golden flower and slightly curved seeds of yellowish to greenish color [2,3, 6-11]. The fennel seeds can be used in the phytotherapy, cosmetic, and food industries, as well as other fields, and the presence of various phytochemicals leads to their continuous growing, i.e., secondary plant metabolites that consist of various bioactive compounds, whose properties are considered beneficial [2, 6-9].

This article aims to present calculations of thermodynamic parameters of the intermediate and final states of essential oil obtained by distillation from fennel fruits. The results can be used to characterize the process. The studies were performed at three steam supply temperatures in order to determine the most suitable one for the process.

2 Materials and methods

2.1 Plant Material

Fennel fruits, harvested in 2021, were used in this study. The essential oil content of the fruits was determined using the apparatus of the British Pharmacopoeia modified by Balinova-Dyakov presented in the paper [12]. The essential oil content of the fruit is 4.32%. The fruits from the fennel were ground in an electric mill. Through sieve analysis, the average size of the ground fruit was determined - 1.125 mm.

2.2 Extraction of essential oil

The fruits were processed in an experimental laboratory plant for steam distillation described in our previous publication [12]. They were pre-moistened with 20% hot water to reduce the duration of the process. For the same reason, the still was filled to 25% of its capacity. The primary distillation waters obtained during the distillation process have an essential oil content of 0.72%.

2.3 Gas chromatography analysis

Analysis of the GC-FID-MS for volatile components in the oil samples was carried out using a gas chromatograph 5890A (Agilent Technologies) coupled to an ionization flame detector (FID) and a mass spectrometry detector MSD 5975C. Compounds were separated on a HP-5 capillary column (5% phenylmethyl polysiloxane, 30 m x 0.25 mm i.d., 0.25 µm film thickness), using the following temperature programmed: 5 min at 40°C, which is then raised with a 5°C/min step up to 300°C, where held for 10 min; the injector and transfer line temperatures are kept at 250°C; an injection volume of 0.1 µL is used with split ratio 1:50. Helium with flow rate of 1 mL/min and an acquisition mass range of 30-600 m/z was used as a carrier gas. All mass spectra were acquired in electron impact (EI) mode with an ionization voltage of 70 eV.

Under this temperature program, a mixture of aliphatic hydrocarbons (C6-C28) (Sigma) was injected into the GC instrument, necessary to estimate the retention index (RI) of the different compounds. Electronic integration measurements with FID were used to obtain the percentage compositions of all compounds.

To identify the compounds, the retention time, mass spectrum, and retention index of the chromatographic peaks were compared with the standard ones. The NIST'08 and ADAMS libraries were used to identify the other volatile components, as shown in [14].

2.4 Thermodynamic parameters

The Gibbs free energy (ΔG) was determined according to the equation from Van't Hoof (1) with variation of temperature presented in [1,4,12-14]:

$$\Delta G = -lnk.R.T \quad (1)$$

The change of free energy of Gibbs in the intermediate state was determined according to the following equation [1,4]:

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad (2)$$

The change of entropy ($\Delta S^{\#}$ and ΔS) of intermediate and final state was defined according to the equation given in literature [1, 4, 12-14].

The change of enthalpy ($\Delta H^{\#}$ and ΔH) of intermediate and final state was determined according to equation (3) [1, 4, 14]:

$$\Delta H^{\#} = E_a - RT \quad (3)$$

3 Results and discussion

As a result of the conducted experiments, carried out with triplicate repetition, primary essential oil was obtained, which was given for analysis.

Table 1 presents the data from our study of the chemical composition of primary essential oil obtained from fennel fruits by steam distillation.

According to GC-MS analysis, the main components in the essential oil of the fennel fruit are: trans-anethole (63.66%), fenchone (19.68%), estragole (methylhavicol) (4.60%), limonene (2.55%), cis-anethole (2.43%), and α-pinene (2.42%). The presented chemical composition of the essential oil of fennel fruits in [15] and the results in this paper confirm the data presented in the literature [2, 14].

According to the obtained values in tables from II to IV for the thermodynamic parameters for the intermediate and final states of the distillation process, it can be concluded that the system is thermodynamically stable. The positive value obtained for the change in enthalpy of the final product means that the process is endothermic, and for it to proceed, energy must be input. Negative values of the Gibbs energy for the intermediate and final state mean that the process occurs spontaneously and irreversibly. The irreversibility of the process was confirmed by negative values of the entropy for the intermediate state and a positive value for the final state. The increase in entropy with increasing time of the process means that it occurs irreversibly.

During the distillation process of essential oil from ground fennel fruits, the hydraulic pressure drop across the raw material was also measured, i.e., the pressure created by the layer, raw material when steam passes through it. Fig. 1 presents the graphical dependence reflecting the pressure drop at the three temperatures. As can be seen from the dependence, the highest pressure drop is at a temperature of 150 °C, and the lowest at a temperature of 130 °C. From 140 °C to 150 °C, the charts are parabolas, which can be explained by the fact that at these temperatures of the superheated steam, the process is over. For the temperature of 130 °C, it can be clearly seen that the highest pressure drop has barely been reached, which means that the process can last longer compared to the other two temperatures.

Table 1. Chemical composition of the primary essential oil

Compound	**Primary essential oil, %**	**RT**	**RI**
Monoterpenes			
α-Pinene	2.32	9.69	930
Camphene	0.39	10.20	943
Sabinene	0.18	10.,98	962
β-Pinene	0.16	11.12	971
Myrcene	0.50	11.56	985
α-Phellandrene	1.04	12.70	1000
Limonene	2.45	12.86	1022
γ-Terpinene	0.34	13.77	1053
Oxygenated monoterpenes			
Fenchone	19.78	14.91	1081
Camphor	0.43	16.54	1139
Terpinen-4-ol	0.15	17.58	1173
Phenylpropanoids			
Estragole	4.70	18.15	1195
cis-Anethole	2.43	19.98	1247
trans-Anethole	63.56	21.03	1280
Other oxygenated compounds			
Anisyl methyl ketone	0.71	23.20	1411
Anisaldehyde	0.37	19.66	1228
Total:	99.51		

RI - relative retention index
RT - retention time

Table 2. Thermodynamic parameters at a temperature of the supplied steam of 130 °C for the intermediate and final state of the essential oil extracted

τ , s	$G^{\#}$, J/mol	$S^{\#}$, J/mol.K	$H^{\#}$, J/mol	G, J/mol	S, J/mol.K	H, J/mol
3600	-5152.99	-40.30	-11094.42	17035.86	61.46	7742.63
7200	-14907.39	-64.50	-11094.42	7281.46	37.27	7742.63
10800	-14739.35	-64.08	-11094.42	7449.49	37.68	7742.63
14400	-14593.95	-63.72	-11094.42	7594.89	38.04	7742.63
18000	-14124.02	-62.55	-11094.42	8064.83	39.21	7742.63
21600	-13849.03	-61.87	-11094.42	8339.82	39.89	7742.63
25200	-11652.94	-56.42	-11094.42	10535.91	45.34	7742.63

Table 3. Thermodynamic parameters at a temperature of the supplied steam of 140 °C for the intermediate and final state of the essential oil extracted.

τ , s	$G^{\#}$, J/mol	$S^{\#}$, J/mol.K	$H^{\#}$, J/mol	G, J/mol	S, J/mol.K	H, J/mol
3600	-371.63	-28.42	-11369.62	10997.98	45.83	7934.69
7200	-4018.64	-37.25	-11369.62	7350.98	37.00	7934.69
10800	-3879.32	-36.91	-11369.62	7490.30	37.34	7934.69
14400	-3793.51	-36.70	-11369.62	7576.10	37.54	7934.69
18000	-3735.34	-36.56	-11369.62	7634.28	37.68	7934.69
21600	-2700.74	-34.06	-11369.62	8668.87	40.19	7934.69
25200	-2226.39	-32.91	-11369.62	9143.22	41.34	7934.69

Table 4. Thermodynamic parameters at a temperature of supplied steam of 150 °C for the intermediate and final state of the essential oil extracted.

τ , s	$G^{\#}$, J/mol	$S^{\#}$, J/mol.K	$H^{\#}$, J/mol	G, J/mol	S, J/mol.K	H, J/mol
3600	-967.08	-29.80	-11644.8	10677.73	44.44	8126.74
7200	-4361.81	-37.83	-11644.8	7283.00	36.42	8126.74
10800	-4030.84	-37.05	-11644.8	7613.97	37.20	8126.74
14400	-3417.18	-35.59	-11644.8	8227.63	38.65	8126.74
18000	-3073.97	-34.78	-11644.8	8570.84	39.46	8126.74
21600	-781.354	-29.37	-11644.8	10863.46	44.88	8126.74
25200	-147.2365	-27.17	-11644.8	11792.05	47.07	8126.74

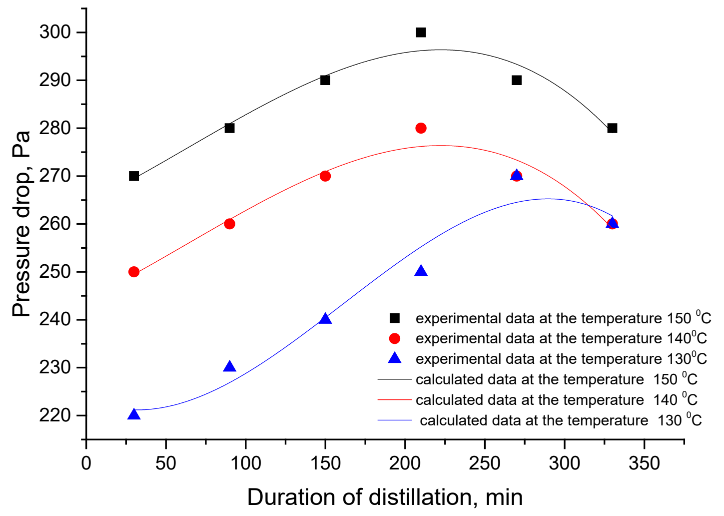

Fig. 1. Pressure drop depending on the temperature of the supplied superheated steam

4 CONCLUSION

In this article, the chemical composition of the essential oil obtained through the distillation process with superheated steam from fennel fruits is determined. The chemical composition of the essential oil contains the following main components: trans-anethole (63.66%), fenchone (19.68%), estragole (methylhavicol) (4.60%), limonene (2.55%), cis-anethole (2.43%), and α-pinene (2.42%).

The thermodynamic parameters of the intermediate and final states were calculated at three different temperatures of the supplied superheated steam. It was found that the system is thermodynamically stable, the process occurs spontaneously and irreversibly, but it is necessary to input energy to carry it out. The pressure created by the layer of raw material during its processing was measured, as a result of which it was found that the process can be completed with a shorter duration at a higher temperature, while at a low steam temperature, the process will have to be extended.

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