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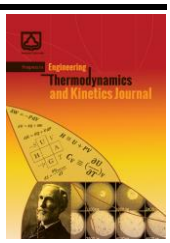

Research Article

Subcritical water extraction of Foeniculum vulgare Mill (Fennel) essential oil

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ABSTRACT

In this study, the essential oil from Foeniculum vulgare Mill seeds (fennel) was extracted using subcritical water and compared to the method of Hydro distillation method. The key component of the essential oil is trans-Anethole. Identification of substances in the essential oil and their quantities was performed through GC and GC/MS analysis. The effects of temperature, mean particle size, flow rate, and extraction time on the amount and quality of subcritical water extraction were studied. To facilitate the experiments and investigate the influence of these parameters and their interactions, the response surface methodology with a central composite design (CCD) was utilized. The optimal conditions for trans-Anethole extraction occurred at a temperature of 125 °C, a mean particle size between 0.5 and 0.71 mm, in 65 minutes, and a flow rate of 25.1 mL/min. The total maximum yield (0.02345 mg essence/g dry sample) obtained under these optimal conditions exceeded that achieved by the Hydro distillation method (0.01322 mg essence/g dry sample).

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1. Introduction

Plants possess a wide variety of bioactive compounds, including lipids, phytochemicals, pharmaceuticals, pigments, flavors, and fragrances. Essential oils and plant extracts are extensively used in the food, medicine, cosmetics, and health industries [1]. This emphasizes the importance of optimally extracting these compounds. One notable plant is fennel. The fennel plant (Foeniculum vulgare Mill) belongs to the Apiaceae family and the parsley genus; it is aromatic, medicinal, and a perennial with feathery leaves found in Europe, North Africa, and Southwest Asia. This plant is cultivated in Iran for its medicinal properties. In many regions of the country, fennel is traditionally used to treat various ailments, including stomach issues and obesity [2]. trans-Anethole, Fenchone, and Limonene are the primary constituents of this plant's essential oil. According to studies, trans-Anethole (70-80%) is the most significant component of the essential oil [3]. One extraction method is subcritical water extraction (SWE). The term 'subcritical water' refers to water at a temperature above the boiling point of 100 °C and below the critical temperature of 374 °C, along with the corresponding pressure. At this temperature and pressure, water remains in its liquid state [4].

SWE is used more than traditional methods due to its advantages, such as high speed, high efficiency, reduction of organic solvents, and environmental compatibility [6, 7]. The pressure levels needed to keep water in the liquid state at 200 °C and 300 °C are 15 bar and 85 bar, respectively. If the pressure at the mentioned temperatures is less than the above value, or in other words, if the pressure reaches below the pressures proportional to the boiling point, supersaturated steam is produced [8]. Under these conditions, water can be used as a suitable alternative to dissolve medium-polarity organic compounds and even non-polar compounds [9]. On the other hand, increasing the temperature increases the penetration rate, reduces the viscosity, and reduces the surface tension of water. If the pressure increases to such an extent that the water remains liquid, these changes will continue beyond the normal boiling point of water to the critical point range of 375 °C and 8.21 bar.

In this case, the polarity of the water is significantly reduced so that it can be applied as an extraction solvent for a wide range of analytes [10]. SWE was first used in 1955 by Basil et al. to extract essential oils from the Rosemary plant [11].

This research study aimed to optimize the extraction of essential oil from fennel seeds using the subcritical water method. Because 70-80% of the total essential oil in fennel seeds is made up of trans-Anethole, the entire essential oil was anticipated as a single component.

This constituent was then measured to enhance the extraction process. Key parameters such as flow rate, extraction time, temperature, and mean particle size were examined during the subcritical water extraction of essential oil. The results of the optimized subcritical water extraction of fennel seeds were compared to the conventional method of hydro distillation extraction.

2. Materials and Methods

2.1. Material

Fennel-dried seeds were purchased in March 2018 from a store in Semnan (Semnan, Iran). High-performance liquid chromatography (HPLC) grade water was employed as an extractant . In the separation of water from the aqueous extracts, n-pentene, Na_2SO_4, and NaCl (Merck, Darmstadt, Germany, >95%, HPLC grade) were employed as an extractor, a drying agent, and an emulsion breaker, respectively.

2.2. Preparation of the sample

Fennel seeds were dried in the shade at room temperature for two days and then stored in polyethylene bags in a -4 °C refrigerator (HARRIS Co., Germany) until the analysis process. The wet content of the fennel seeds was 8% (based on the dry weight). Before conducting the experiments, the dried samples were crushed using a laboratory mill. The powder was prepared with standard sieves with mesh sizes less than 0.25 mm, between 0.25 and 0.5 mm, between 0.5 and 0.71 mm, between 0.71 and 1 mm, and greater than 1 mm.

Sample preparation was performed just before extraction to prevent losses of volatiles, and the samples were stored in five glass containers.

2.3. Hydro distillation method

Hydro distillation of 100 g of grounded Fennel without leveling was done and poured directly into 1000 mL of deionized water in a Clevenger, and after 3 hours and 30 minutes, the distillation was completed. About 2 mL of essential oil was collected. The essential oil was dried using anhydrous Na_2SO_4 and stored in a dim cut-glass flask at 4°C until analysis.

2.4. Subcritical water extraction method

SWE was performed in a laboratory apparatus shown in Figure 1.

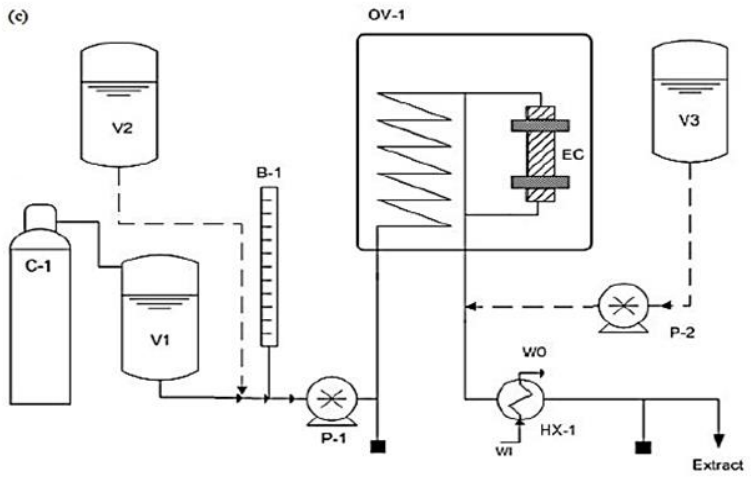

Figure 1: The extraction process diagram with subcritical water.

Includes Burette (B), nitrogen container (C), extraction chamber (EC), a heat exchanger (HX-1), Oven (OV-1), pumps (P-1, P-2), water reservoir (V-1), solvent reservoir (V-2), solvent wash reservoir (V-3), Water input (WI), and water output (WO) [12].

To remove dissolved oxygen from water, HPLC water was first placed in an ultrasonic bath for 20 minutes and then deoxygenated for 30 minutes in the feed tank of the extraction apparatus using subcritical water with a nitrogen gas flow. An HPLC pump (BFRL Company, SY-8100 series, Germany) was used to transfer the water into the system.

A burette was also installed to control the pump's operation, and a stainless steel heating screw measuring 3 meters in length was included for additional heating. The extraction vessel measured 520 mm in length and 52 mm in diameter. In each test, 2 g of ground fennel was placed inside longitudinal cloth packs and positioned within the test vessel. The furnace operated at 210 °C, allowing for measurable and observable inlet and outlet temperatures of the extraction vessel, with adjustable pressure. After the extraction process, a heat exchanger was placed at the furnace outlet to lower the extracted temperature. It should be noted that during extraction, 20 mL of liquid, approximately the size of the device's tubes, was discarded, and the resulting extract was collected in a glass sample container.

In all experiments, a specific volume of extract was removed to isolate the essential oil. To disrupt the colloidal bond, a 25% solution of salt extract was prepared and separated using liquid-liquid extraction with typical pentane solvent in a 1:2 ratio across two stages of the organic phase The resulting organic phase was placed in a test tube for complete separation of the material from the essential oil, performed in two stages in a centrifuge: the first stage lasted 15 minutes at 4000 rpm. In contrast, the second stage lasted 5 minutes at 4000 rpm.

The essential oil obtained was fully exposed to air for 4 to 5 hours in each experiment to ensure complete separation from normal pentane. After this complete separation, 2 mL of normal pentane was added to the essential oil, which was then immediately poured into the sample container and stored in the refrigerator until injected into a gas chromatographic analyzer.

2.5. Central Composite Design

To optimize the main parameters of subcritical water extraction for essential oils from fennel seeds, a central composite design (CCD) was employed. The CCD method employs a two-level factorial design, comprising central and axial points. In this approach, each factor features five distinct levels: three within the range and two outside of it.

A quadratic model, representing a second-order polynomial, was used to determine the optimal point, with its equation presented as follows:

$$Y = \beta_o + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j$$

Where the response (yield) is Y, the intercept coefficient, the linear coefficient, the quadratic coefficients, and the interactive regression coefficient are 0, i, ii, and ij, respectively. Xi and Xj represent the independent variable levels [13].

Four process parameters at five different levels to evaluate the essential oil yield were studied which included temperature (90, 107, 5, 125, 142, 5, 160 °C, mean particle size (less than 0.25 mm, between 0.25 and 0.5 mm, between 0.5 to 0.75 mm, between 0.75 to 1 mm and greater than 1 mm), flow rate (0.5, 0.88, 1.25, 1.63 and 2 mL/min) and time (40, 52.5, 65, 77.5 and 90 min). In all experiments, 1 g of Fennel seeds, the ratio of sample to co-packing was 1:1.5, and 20 bar pressure was applied.

The essential oil yield (w/w) in both extraction methods was calculated with the following relation, based on percentage:

$$yield\ (\%) = \frac{amount\ of\ essential\ oil\ (g)}{amount\ of\ dry\ sample\ (g)} \times 100 \qquad (1)$$

2.6. Analysis by gas chromatography (GC)

The analysis was performed by gas chromatography in the analysis laboratory. The devices used had the following characteristics: a GC device (Series 6100, ACME), which utilized a column (TRB-WAX) with a length of 60 meters, an internal diameter of 32 micrometers, and a polyethylene glycol film thickness of 25 micrometers.

The operating conditions of the device were as follows: 50-230 °C, temperature rate of 3 °C per min, helium carrier gas with a purity of 99.99% (ROHAM company, Tehran, Iran), with a separation ratio of 1:100 and a flow rate of 5 mL/min.

2.7. Analysis by gas chromatography-mass spectrometer (GC-MS)

GC/MS analysis was achieved under the following conditions: Varian, Walnut Creek, USA, DB-5 silica column with a length of 60 m, internal diameter of 25 μm, and film thickness of 25 μm, and software. The operating conditions of the device were as follows: Ionizing energy 70 eV, mass range 40-400 amu, and EI scanning method, under temperature conditions of 40 to 200 °C with a temperature velocity of 3 °C per min and a separation ratio of 1:30.

3. Results and discussion

The maximum yield (0.02345 mg essence/g dry sample) obtained at the optimal conditions was more than that achieved by the Hydro distillation method (0.01322 mg essence/g dry sample). The GC-MS results showed that in Fennel essential oil, besides t-Anethole (73.89 %), Fenchone (9.14 %), Limonene (6.01 %), Methyl chavicol (2.96 %), Carvone (1.93 %), and α-pinene (0.8 %) were the main and major components. GC-MS results are shown in Figure 2. Different substances identified for the essential oil obtained by the Hydro distillation and subcritical water extraction are given in Table 1.

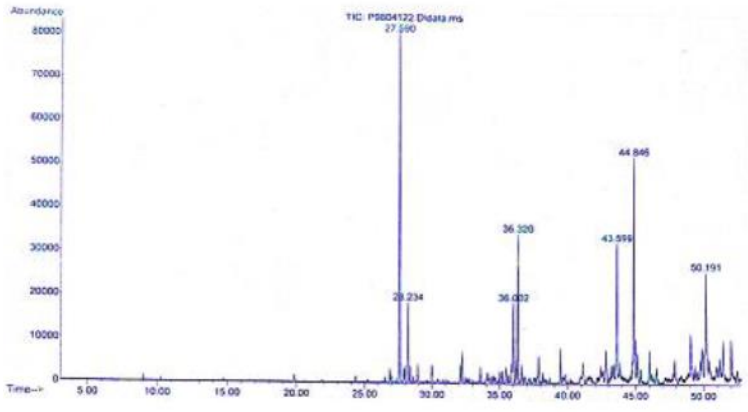

Figure 2: GC/MS analysis for subcritical water extraction for 2 g of grounded Fennel.

(Mean particle size between 0.5 and 0.71 mm, temperature 125 °C, flow rate 1.25 ml/min, extraction time 65 min).

Table 1. Different substances were identified for the essential oil obtained by the distillation and subcritical water extraction at a mean particle size between 0.5 and 0.71 mm, temperature 125 °C, flow rate 1.25 mL/min, and extraction time 65 min.

Components	Hydro distillation (%)	SWE (%)
α-pinene	0.8022	-
Sabinene	0.2785	-
β-pinene	0.528	-
p-cymene	0.7345	-
Limonene	6.0115	3.8243
1,8-cineole	0.2022	-
(z)-β-ocimene	0.2688	-
γ-teripene	-	4.1274
Fenchone	9.1433	0.508
Comphor	0.1893	-
Methyl chavicol	2.9612	0.3759
Carvone	1.9295	-
p-Anis aldehyde	0.4862	-
t-Anethole	73.8921	88.8957

The experimental results for the four variables in CCD are shown in Table 2.

Table 2. The experimental results used four variables in CCD.

Exp.	Temperature (°C)	Flow rate (ml/min)	Time (min)	P-size (mm)	Yield (%)
١	١٠٧,٥	١,٦٣	٧٧,٥	٠,٤٤	٠,٧٣٨٢
٢	١٢٥	١,٢٥	٦٥	٠,٦٣	٠,٦٨٣٢
٣	١٠٧,٥	٠,٨٨	٥٢,٥	٠,٨١	٠,٣٩١٨
٤	١٤٢,٥	٠,٨٨	٧٧,٥	٠,٨١	٠,٧٥٦٣
٥	١٢٥	١,٢٥	٤٠	٠,٦٣	٠,٦٥٢٢
٦	١٢٥	١,٢٥	٦٥	٠,٢٥	٠,٥٤٣٤
٧	١٤٢,٥	٠,٨٨	٥٢,٥	٠,٤٤	٠,٥٩٧٨
٨	١٤٢,٥	١,٦٣	٧٧,٥	٠,٤٤	٠,٩٧٧٢
٩	٩٠	١,٢٥	٦٥	٠,٦٣	٠,٤٢٣٩
١٠	١٢٥	١,٢٥	٩٠	٠,٦٣	٠,٨٣٥٢
١١	١٠٧,٥	١,٦٣	٥٢,٥	٠,٨١	٠,٥٣٢٦
١٢	١٢٥	١,٢٥	٦٥	٠,٦٣	٠,٧٠٦٥
١٣	١٤٢,٥	٠,٨٨	٥٢,٥	٠,٨١	٠,٥٦٥٢
١٤	١٠٧,٥	٠,٨٨	٧٧,٥	٠,٤٤	٠,٥١٠٨
١٥	١٢٥	٢	٦٥	٠,٦٣	٠,٧٥
١٦	١٢٥	١,٢٥	٦٥	٠,٦٣	٠,٧٠٦
١٧	١٤٢,٥	١,٦٣	٥٢,٥	٠,٨١	٠,٦١٢٧
١٨	١٢٥	١,٢٥	٦٥	٠,٦٣	٠,٧١٥٢
١٩	١٤٢,٥	٠,٨٨	٧٧,٥	٠,٤٤	٠,٧٩٣٤
٢٠	١٠٧,٥	١,٦٣	٥٢,٥	٠,٤٤	٠,٧٦٠٨
٢١	١٢٥	٠,٥	٦٥	٠,٦٣	٠,٤١٣
٢٢	١٠٧,٥	٠,٨٨	٧٧,٥	٠,٨١	٠,٣٢١٧
٢٣	١٦٠	١,٢٥	٦٥	٠,٦٣	٠,٨٦٩٨
٢٤	١٠٧,٥	٠,٨٨	٥٢,٥	٠,٤٤	٠,٤٧٨٢

٢٥	١٠٧,٥	١,٦٣	٧٧,٥	٠,٨١	٠,٥٧٣
٢٦	١٢٥	١,٢٥	٦٥	٠,٦٣	٠,٧٠٦٨
٢٧	١٢٥	١,٢٥	٦٥	١	٠,٣١٥٢
٢٨	١٤٢,٥	١,٦٣	٥٢,٥	٠,٤٤	٠,٦٢٥٦
٢٩	١٤٢,٥	١,٦٣	٧٧,٥	٠,٨١	٠,٨٥٨٦
٣٠	١٢٥	١,٢٥	٦٥	٠,٦٣	٠,٧١١

A comparison of the highest percentage of trans-Anethole was used to identify the optimal conditions in the extraction method with subcritical water, which occurred at a temperature of 125 °C, an average particle size between 0.5 and 0.71 mm, and a flow rate of 1.25 mL/min in 65 min. It should be noted that in all experimental runs, the pressure was set to 20 bar to maintain the water in its liquid state. According to the ANOVA table, only parameters with a p-value of less than 0.0001 were considered for the model, and other parameters were removed from the model. The model was accepted. The following model was obtained based on the effective parameters:

$$\text{yield} = +0.77552 - 4.45916\text{E} - 003 \times \text{Temp} + 1.18564 \times \text{Q} - 0.045684 \times \text{t} + 1.31896 \times \text{P} - \text{size} + 2.86829\text{E} - 004 \times \text{Temp} \times \text{t} - 1.81425 \times \text{P} - \text{size}$$

Where Temp is the extraction temperature (oC), Q is the flow rate (mL/min), t is the extraction time (min), and P-size (mm) is the mean particle size range. The experimental data were fitted to the response equation with an R^2 value of 0.9804. Also, different values of R^2_{adj} and R^2_{Pred} were 0.9621 and 0.8906, respectively. The effect of four process parameters on the amount of essential oil extraction was then investigated. The relative standard deviation percentage (%RSD) for extraction yields was calculated based on the measured peak areas. The %RSD values ranged from 5 to 18%.

3.1. Effect of temperature

Temperature is the most critical parameter in extraction with subcritical water, and a change in water polarity is the most crucial effect on the extraction process [14]. Water at temperatures above 200 °C can act as a solvent for non-polar compounds and reduce tissue adhesion between particles. By reducing the viscosity, the solvent penetrates better into the plant tissue [15]. Increasing the temperature due to increasing solubility causes an increase in the amount of essential oil extraction. However, at high temperatures, unwanted paraffin compounds in the plant may be added to the essential oil [16]. Increasing the temperature destroys the bioactive compounds and darkens the extract. The opacity of the extract is attributed to the disintegration of plant tissue and its dispersion in the extract [17]. Therefore, the temperature should be high enough to facilitate the extraction of the target compound, but to prevent the extraction of unwanted compounds [18]. In Figure 3, the effect of the extraction time and temperature on the extraction yield at a constant flow rate of 1.25 mL/min and a mean particle size of 0.63 (between 0.5 and 0.75 mm) is presented. It demonstrates that the extraction yield improved with increasing temperature up to 142.5 °C. Due to device restrictions, tests were not possible at higher temperatures .

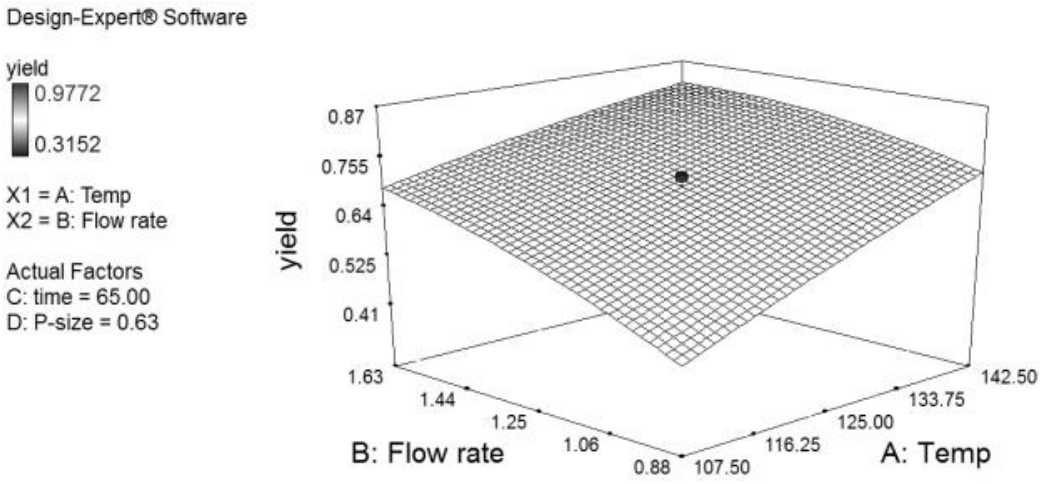

Figure 3: The extraction yield versus the simultaneous effect of temperature (A) and flow rate (B).

3.2. Effect of mean particle size

The mean particle size of the plant is one of the critical parameters in the extraction rate. Different plant tissues differ in chemical and physical properties, type of composition, or particle diameter. These factors affect the retention and adsorption properties of the target material. For example, reducing the particle size improves extraction efficiency due to enhanced mass transfer. But if the mean particle size is too small, the adhesion of the particles to each other reduces the extraction efficiency. Additionally, reducing the particle size is time-consuming, and there is a risk of destroying the compounds during crushing [19]. If it is too large, the process will not be able to extract the essential oils fully.

Figure 4 demonstrates that until the mean particle size was 0.44 mm (particle size range was between 0.5 and 0.71 mm), the essential oil extracted augmented with declining particle size. This suggests that the mass transfer of crucial oil components within the plant seed governs the extraction process.

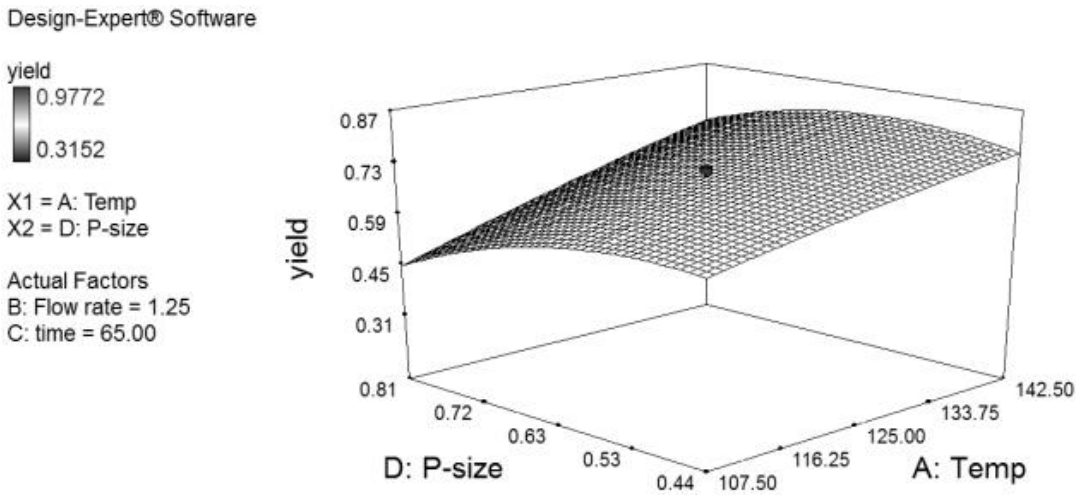

Figure 4: The extraction yield versus the simultaneous effect of temperature (A) and particle size (D).

3.3. Effect of flow rate

One of the factors affecting the amount of essential oil extraction in the SWE process is the flow rate. Typically, the flow rate is selected between 1 and 4 ml/min [20]. The effect of the mean particle size and flow rate on the extraction yield at a constant temperature of 125 ^{o}C and time of 65 min is shown in Figure 5. As displayed in Figure 4, the extraction yield improved with the increasing water flow rate. Therefore, the mass transfer of the essential oil from the solid plant surface to the water phase controls most of the extraction process.

At low flow rates, the extraction rate is low, but the extract is more concentrated. Conversely, at high flow rates, the extraction rate is high, but the extract is more diluted [21, 22].

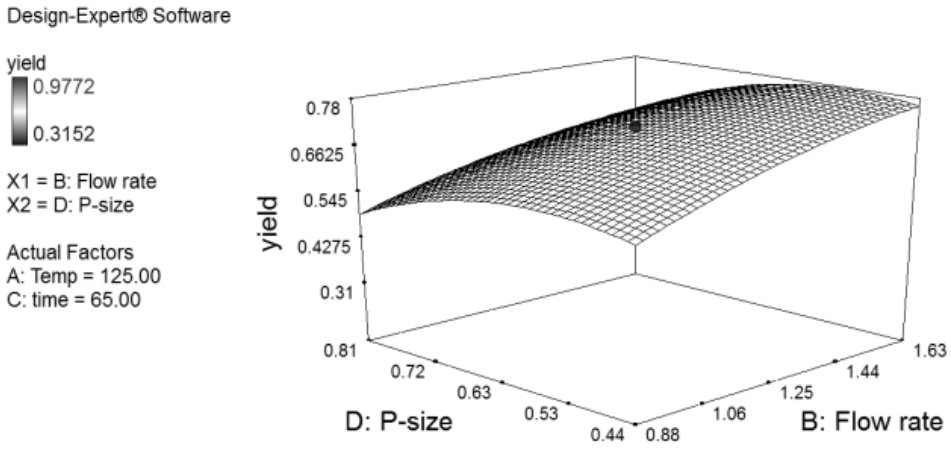

Figure 5: The extraction yield versus the simultaneous effect of flow rate (B) and particle size (D).

3.4. Effect of extraction time

Another influential parameter in extraction with subcritical water is time. In general, the extraction of essential oil increases with increasing time. But it should be borne in mind that if the time is too short, the essential oils may not be able to be extracted. On the other hand, if the reaction time is too long, substances may be added to the extract to form a new combination with the critical substances in the essential oil. Figure 6 shows the effect of two parameters, time and mean particle size. The extraction time is powerfully dependent on the nature of the network and analytes, as well as the extraction temperature [23]. For extracting materials from plant samples or examining environmental samples, the dynamic mode takes 5 minutes to 2 hours, and the static method takes 5 to 10 minutes, both of which have good efficiency. As the extraction time increases, efficiency also increases and tends to reach a constant value [24].

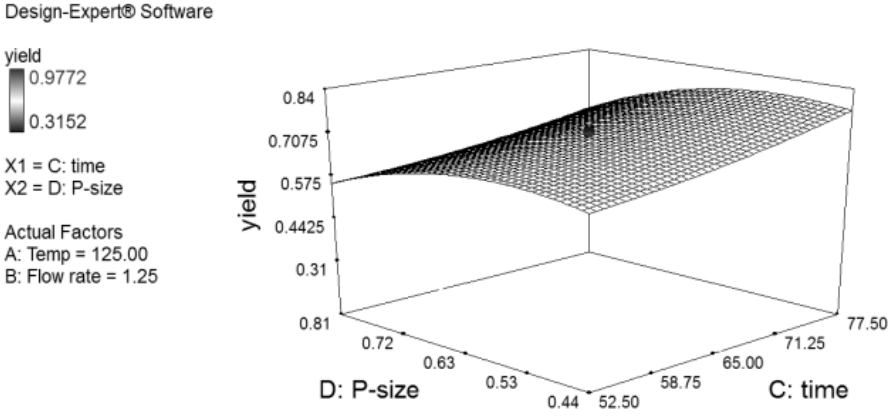

Figure 6: The extraction yield versus the simultaneous effect of time and particle size (D).

4. Conclusion

The water extraction method using subcritical temperatures is a new approach that has been considered today due to its speed, reduced need for organic solvents, high selectivity, and environmental compatibility. This study aimed to extract the essential oil of the Fennel plant using liquid water extraction at subcritical temperatures, a novel method. The extraction method using liquid water at subcritical temperatures was compared with the water distillation method, and the optimal conditions for trans-Anethole extraction were identified. Additionally, the parameters affecting extraction under subcritical water conditions were investigated. The results show that the extraction method at subcritical water is faster than Hydro distillation, and its essential oil has a higher quality. Additionally, by adjusting the operating conditions, the quality of the essential oil can be altered, whereas this is not possible in Hydro distillation. It is also clear from the procedures that the temperature and time parameters of extraction, as well as the flow rate and temperature, had the most significant interaction effect in this experiment, while the least significant interaction effect was related to two parameters: time and mean particle size.

Acknowledgments

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