Supercritical Carbon Dioxide Extraction of Essential Oil From Iranian Lavender Flower

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ABSTRACT

Essential oil was extracted from Iranian lavender flowers using supercritical carbon dioxide in a semicontinuous system. The extraction procedure was composed of static and dynamic operations. In this study, a statistical experimental technique based on "Central Composite Design" was applied in order to evaluate and optimize the operating conditions. The effect of important parameters on extraction efficiency such as supercritical pressure, temperature, and static and dynamic periods were investigated in the range of 80-120 bar, 313-333 K, 10-30 min, and 60-140 min, respectively. The results of GC-FID analysis of the extracted samples were utilized in order to determine the extraction yield of four essential constituents such as (1) Camphor, (2) Fenchone, (3) Linalyl acetate, and (4) Linalool. Furthermore, the overall extraction yield was also investigated. The maximum extraction yield was obtained at optimum conditions of 100 bar, 323 K, 10 min (static), and 100 min (dynamic) for semicontinuous process. Overall, the experimental results of this research indicated that supercritical fluid extraction is a viable technique for production of Camphor, Fenchone, Linalyl acetate, and Linalool applicable in pharmaceutical and cosmetic industries.

INTRODUCTION

A volatile mixture of terpenes and their derivatives is generally responsible for the characteristic fragrance of vegetable matters. The extraction of essential oil from flowers and leaves represents an attempt to isolate this mixture while preserving the original composition that produces the natural fragrance. Unfortunately, the techniques usually adopted, such as steam distillation and solvent extraction, suffer several limitations in extracting and preserving the composition of natural fragrances [1]. The shortcomings of the aforementioned methods are as follows : (1) They can produce the degradation of thermolabile compounds, hydrolysis of water sensitive compounds, and solvent contamination, (2) steam distillation can produce an incomplete collection of compounds responsible for the fragrance, and (3) since steam distillation is based on the evaporation of volatile compounds induced by steam [2], thus, compounds with low vapor pressure are not completely extracted by this technique. Supercritical fluids have proved to be effective solvents for applications in chemical, petrochemical, pharmaceutical and environmental processes. They have liquid-like densities, gas-like viscosities and diffusivities at least an order of magnitude higher than that of normal liquid, which may result in superior mass transfer characteristics. Further, the solvent density, and hence the solvent effectiveness, can be controlled by small changes in temperature and pressure. Carbon dioxide is usually preferred as a supercritical fluid, because it is non-toxic and non-flammable, has a low critical temperature of 304.4 K and a moderate critical pressure of 72.8 bar [3–4]. The main objective of this study was to extract essential oil from Iranian lavender flowers using supercritical carbon dioxide in a semicontinuous and a newly

developed batch system for production of Camphor, Fenchone, Linalyl acetate, and Linalool used in pharmaceutical and cosmetic industries.

MATERIALS AND METHODS

In order to carry out the objectives of this study, the semicontinuous system shown in Figure 1 was used. This system operates at a temperature range of 25–200°C with a maximum pressure of 500 bars. The system is constructed so that any non-corrosive or corrosive gas can be used as the supercritical fluid. The supercritical extraction system used in this study is shown in Figure 1. The experimental setup for the supercritical extraction system is composed of the following: (1) CO_2 cylinder, (2) molecular sieve column, (3) metal porous filter, (4) cooler circulator, (5) HPLC pump, (6) valve, (7) oven with PID temperature controller (8) coil preheater, (9) injection valve, (10) extraction column, (11) washing valve, (12) valve, (13) back pressure regulator, (14) extracted material/solvent collection vessel.

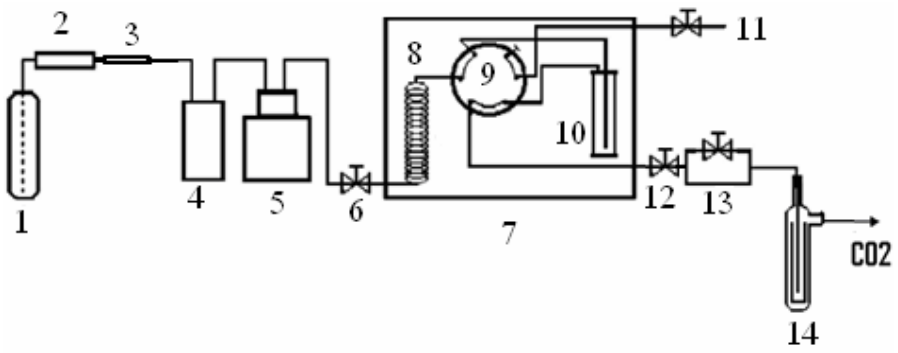

Figure 1. Schematic diagram of supercritical extraction system

In order to increase the purity of the CO_2 (99.95%; Zamzam), which is stored in a CO_2 cylinder (1), it is passed through a column of molecular sieve beads (2) and metal porous filter (3). Then, CO_2 is cooled down to 0 °C in a cooler circulator (4), and subsequently charged by a feed pump (Jasco) (5). A valve (6) is placed at the effluent of the pump, and thus, the CO_2 stream is easily controlled and saved properly for further use. Carbon dioxide is heated before entering the extraction column (10) by using a coil preheater (8) that is placed in an oven (7). After reaching the corresponding supercritical fluid conditions inside the extraction column, the static time is provided for extraction process by closing the valve (12). After carrying out the static extraction, the dynamic extraction with constant volumetric flow rate (1 mL/min) of CO_2 is started via opening the valve (12). At this stage, the system pressure is controlled and monitored by a back pressure regulator (Tescom) (13) and a high-pressure pump. The stainless steel extraction column (height = 12.5 cm, inner diameter (ID) = 0.9 cm, and outer diameter (OD) = 1.3 cm) (10) fitted with cotton wool at the inlet and outlet is manually charged with lavender flower (Isfahan) and glass beads with a mesh size of 20-40 in a ratio of 40–60% (w/w), respectively. Firstly, carbon dioxide is charged into the extraction column while the pump is set at the selected operating pressure and the desired temperature is obtained via the oven and preheater. After reaching the appropriate pressure and temperature in the column, the pump is turned off and isolated with a shut-off valve. Subsequently, a

period of static extraction time is allowed for SC–CO_2 to dissolve the essential oil and then by passing the CO_2 at a flow rate of 1 mL/min, the dissolved oil via static and dynamic extraction is discharged from the column, trapped, and collected with 10 mL of ethanol (Merck) in the collection vessel (14). The essential oil contained in the extracted samples was kept in the refrigerator for further Gas Chromatography-Flame Ionic Detector (GC-FID) analysis.

Results and Discussion

A statistical experimental design based on "Second Order Composite Design" was planned with a fixed flow rate. The independent effective parameters (temperature, pressure, dynamic time, and static time) on the dependent parameter of extraction yield (Y) for each component were coded as x_1, x_2, x_3, and x_4, respectively. These independent parameters were investigated in five levels (-2,-1, 0, 1, and 2). The MINITAB software package was used for design and evaluation of the four independent variables at five levels on the extraction yield (response) according to the following equation (1). Table 1 shows the chosen ranges for different parameters at five levels and the obtained experimental results of 31 runs are shown in Table 2.

$$Y = \beta_0 + \sum \beta_j X_i + \sum \beta_{jj} X_{j2} + \sum \beta_{jk} X_j X_k \quad (1)$$

Where Y = Response variable, β_0 = intercept, β_j = linear coefficients, β_{jj}= squared coefficients, β_{jk}= interaction coefficients, X_i, X_{j2}, X_j X_k = level of independent variables). The two star points of -2 and +2 are calculated from the following equation:

$$\alpha = \text{star point} = \pm (2^{\text{parametes}})^{1/4} = \pm (2^4)^{1/4} = \pm 2 \quad (2)$$

Table 1: Range of values for the response surface methodology

	Levels				
variables	-2	-1	0	1	+2
Temperature (^oC)	40	45	50	55	60
Pressure (bar)	80	90	100	110	120
Dynamic time (min)	60	80	100	120	140
Static time (min)	10	15	20	25	30

A second-order polynomial equation is proposed for prediction of extraction yield as a function of independent variables as follows:

$$Y = -206.325 + 4.284\ T + 2.080\ P + 0.891\ t_d + 1.016\ t_s - 0.084\ T^2 - 0.013\ P^2 - 0.003\ t_d^2 - 0.025\ t_s^2 + 0.028\ T \times P + 0.006\ T \times t_d - 0.005\ P \times t_d \quad (3)$$

Where Y, T, P, t_d, and t_s were the extraction yield, temperature, pressure, dynamic time, and static time, respectively.

The experimental data were analyzed by response surface design (RSD) using the Minitab software. The results of the statistical analysis including, the estimated regression coefficients, t-values (t- test) and p-values of extraction yield are shown in Table 3.

Table 2: Experimental matrix design for five-level-four factors central composite design

run	Temp. (^oC)	Press. (bar)	Dynamic time (min)	Static time (min)	Extraction Yield
1	50	100	60	20	70.11
2	50	100	140	20	89.92
3	45	110	120	25	86.88
4	50	80	100	20	69.16
5	55	110	80	25	75.11
6	50	100	100	20	83.32
7	55	110	120	25	85.94
8	45	110	80	25	82.85
9	55	110	120	15	84.02
10	50	100	100	20	83.51
11	50	100	100	20	83.49
12	40	100	100	20	77.24
13	45	110	120	15	84.76
14	50	100	100	20	83.28
15	55	90	120	25	72.87
16	60	100	100	20	75.35
17	45	90	120	15	82.99
18	55	90	80	25	63.91
19	45	90	80	15	71.21
20	50	120	100	20	90.31
21	45	90	120	25	84.88
22	55	90	120	15	70.76
23	45	90	80	25	73.18
24	55	90	80	15	62.24
25	50	100	100	20	82.93
26	50	100	100	10	79.33
27	50	100	100	20	83.41
28	55	110	80	15	73.30
29	45	110	80	15	83.67
30	50	100	100	20	83.11
31	50	100	100	30	85.17

The analysis of variance (ANOVA) shows the suitability of the fitted models. The adjusted R^2 of the extraction yield was calculated to be 85.1%. This shows that the developed model for prediction of the extraction yield only differs ±14.9% from the experimental data. The linear regression coefficient, R^2 for the extraction yield was calculated 92.1% that is the indication of good performance for the developed model. In view point of the statistical results (ANOVA) with confidence level of 80%, the effect of each term in the yield model could be significant provided that it's *p*-value be smaller than 0.633 (p-value<0.633). Table 3 shows the degree of significance of different terms of (1) linear, (2) squared, and (3) interaction. According to the obtained results for the coefficients and *p-value* in Table 3, it can be concluded that the linear, quadratic, and interaction terms have strong, very strong and weak

influence on extraction yield, respectively. It should be noted that the static time with weak effect is an exceptional case for the quadratic terms. Among the interaction terms, interaction between static time with temperature, pressure and dynamic time have no effect whatsoever on the extraction yield.

Table 3: The regression coefficients, t-test and significance *p-value* for the model estimated by Minitab software

Term	Yield of extraction		
	Coefficient	*p*-value	*t*-value
Constant	-206.325	0.125	-1.620
T	4.284	0.133	1.583
P	2.080	0.144	1.538
t_d	0.891	0.147	1.526
ts	1.016	0.633	0.444
T^2	-0.084	0.001	-3.986
P^2	-0.013	0.031	-2.361
t_d^2	-0.003	0.041	-2.229
t_s^2	-0.025	0.258	-1.174
T × P	0.028	0.062	2.004
T × t_d	0.006	0.371	0.921
T × t_s	0.006	0.838	0.208
P × t_d	-0.005	0.225	-1.262
P × t_s	-0.003	0.821	-0.230
t_d × t_s	0.002	0.767	0.301

The trend of effective parameters on yield are investigated and the final optimum results are provided. The first parameter is the isobaric temperature which has a direct effect on the physicochemical properties of CO_2 (density, diffusion, viscosity, and surface tension) and the extracted compounds (solute vapor pressure). The effect of temperature on the extraction yield is shown in Figure 2. Enhancement of extraction yield is observed via increasing temperature in the range of 40-49 ^oC, in which higher solute solubility effect due to increased vapor pressure overcomes the effect of the solvent density decrease. Beyond 49 ^oC, the retrograde solubility prevails and therefore, the effect of density decrease overcomes the influence of increased vapor pressure of solute. Thus, lower extraction yield is obtained in the range of 49-60 ^oC. Figure 2 shows the effect of pressure on the extraction yield in the range of 80-120 bars. It is observed that the extraction yield is enhanced by increasing pressure up to 112 bars due to higher density; in other words, better interaction between solvent and matrix, and solvation capabilities and also higher mass transfer driving force provide an appropriate medium for leaching process to take place. Beyond 112 bars, saturation limitation occurs and thus, a constant trend of extraction is obtained up to 120 bars. These results are compatible with the results of other studies [3-4]. It is important to maximize the contact of the supercritical fluid with the sample material in order to enhance the efficiency of SFE. Several variables that influence the solvent contact time with sample material include flow rate, SFE time, and SFE mode (static with no flow-through or dynamic with flow-through). The static extraction prior to dynamic extraction improved the extraction recoveries in SFE extraction. Samples were held in the static extraction mode in the range of 10–30 min, followed by a dynamic extraction in the range of 60–140 min at the constant flow rate of 1 ml/min.

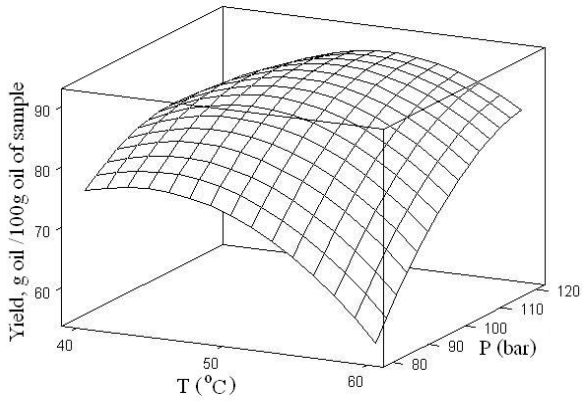

Figure 2. Response surface of extraction yield vs. temp. and pressure with t_d = 123min, t_s = 22 min

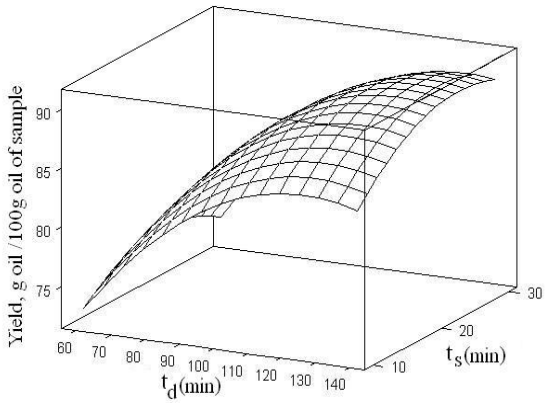

Figure 3. Response surface of extraction yield vs. dynamic and static time at the T = 49°C, P = 112 bar

In this study, static extraction is increased up to 22 min and becomes constant in the range of 22-30 min. The observed extraction efficiency can be explained in terms of higher mass transfer driving force up to 22 min. Using dynamic extraction, higher mass transfer driving force at the beginning provides a suitable condition for extraction and this continues up to 123 min and after that a constant mode of extraction is observed due to very low essential oil concentration on the matrix. The results indicate that the extraction time strongly depends on the extraction temperature, pressure and the nature of the matrix and analytes. The optimum operating conditions to achieve maximum extraction yield (90%) for temperature, pressure, dynamic time, and static time were 49 °C, 112 bar, 123 min, and 22 min, respectively.

CONCLUSION

The experimental supercritical extraction of essential oil from Iranian lavender flower was carried out and the results demonstrated that SCF extraction is a viable technique to be applied in pharmaceutical and cosmetic industries. Utilizing a statistical experimental design based on "Second Order Composite Design" to optimize the operating conditions revealed that maximum extraction yield of 90% can be achieved at optimum operating conditions of temperature, pressure, dynamic time, and static time.

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