Optimizing the Supercritical Carbon Dioxide Extraction of Hibiscus Flower Essential Oil using Response Surface Analysis

Tahani Y. A. Alanazi
Department of Chemistry, College of Science, University of Ha'il, Saudi Arabia
ty.alanazi@yahoo.com (corresponding author)

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ABSTRACT

The development of Supercritical Fluid Extraction (SFE) has opened the door to the harvesting of plants for a wide range of chemical compounds. This study distilled essential oil from hibiscus flowers utilizing the supercritical CO_2 method. Different extraction parameters, including pressure (100-300 bar) and temperature (300-350 K), were studied to visualize how they affected oil recovery. Response surface analysis was used to fine-tune the extraction process. The chemical composition of the recovered oil was analyzed by Gas Chromatography-Mass Spectrometry (GC-MS). According to the findings, 13.11% per 80 g of dry flowers is the ideal oil extracted from Hibiscus flowers, using SFE at 200 bar pressure and 325 K extraction temperature. Six compounds were provisionally identified in the extracted oil from hibiscus flowers under optimum SFE conditions.

Keywords-essential oil; response surface analysis; hibiscus flower; Supercritical Fluid Extraction (SFE); Gas Chromatography-Mass Spectrometry (GC-MS)

I. INTRODUCTION

Essential oils, also called volatile or ethereal oils, are fluid mixtures obtained by distilling aromatic plant materials [1]. In manufacturing, volatile oils with aromatic properties are known as "fundamental oils". Phenols, esters, alcohols, ketones, aldehydes, and hydrocarbons are all part of the complex chemical makeup of these oils [2]. Essential oils extracted from numerous plants are commercially available [3]. Several discussions have been held about the biological activity of essential oils [1-4]. An example is olive leaf oil, which has been found to have a strong and high antioxidant capacity [5].

The Malvaceae family encompasses many well-known evergreen and grassy plants, including the popular Hibiscus rosa-sinensis. This plant can grow to a width of 1.5-3.0 m (5-10 ft) and a height of 2.5-5.0 m (8.0–16 ft). Most hibiscus trees originate in tropical regions, such as Southeast Asia, Australia, and Africa. Nowadays, this plant can be found almost anywhere in the world. Hibiscus flowers are used predominantly for decorative purposes. For example, flowers are often cut in half and used to create laurel wreaths. The medical, cosmetic, decorative, and industrial applications of hibiscus have increased its market value [6-7]. Its leaves, roots, and flowers have medical properties, serving as a laxative, an aphrodisiac, and a contraceptive. The oil extracted from the hibiscus flower acts as a stimulant, cough suppressant, germicide, and muscle relaxant [7]. It contains hydrocarbons and glycerides of various types. The chemical compounds found in this oil include eugenol, cis-jasmone, linalool, benzyl acetate, benzyl alcohol, farnesol, isophytol, benzyl benzoate, acid derivatives, phytol, and geraniol [8]. The oil from this flower is beneficial for depression, migraines, sensitive skin, and fatigue, among other conditions [9]. Different types of the same plant, grown for its flowers or essential oil, include Hibiscus schizopetalus, Hibiscus rosa-sinensis, Hibiscus mutabilis, Hibiscus sabdariffa, and Hibiscus tiliaceus [6]. Hydro-distillation, solvent extraction, and maceration are adopted to extract oil from the hibiscus plant. However, these methods entail certain drawbacks, including decreased oil yield [10-11].

There are several methods to extract hibiscus flower oil, involving the liquid-liquid extraction method [12], where the flowers are soaked for a very long time and require special solvents, but it is a more restrictive and expensive method and its results may be unsatisfactory. This study used the cutting-edge method of supercritical liquid extraction. Supercritical Fluid Extraction (SFE) offers a blend of advantages, including selectivity and efficiency due to the adjustable density of supercritical fluids, and environmental friendliness through the use of non-toxic and recyclable CO_2. Furthermore, low-temperature operations benefit the extraction of thermally labile compounds, and the high purity of extracts with minimal residual solvents makes them suitable for products intended for human consumption. However, SFE faces limitations, such as high equipment costs, restrictions on volatile and semivolatile compounds, operational complexity that requires specialized knowledge, and scaling challenges for industrial applications, which affect its broader adoption. The state of a supercritical liquid can be altered by changing the temperature and/or pressure. In the health and medical industries, this is crucial. Due to its specific physical properties, such as low temperature and moderate pressure, CO_2 is used in supercritical liquid extraction [13]. It has also been claimed that this technique produces a higher yield than either hydro-distillation or steam. However, the high price of the necessary hardware limits the applications of SFE to only the most fundamental mechanical parameters [14]. Essential oils of Apricot [15], Myrtle [16], Palm [17], Juniperus [18], Soybeans [19], Rosemary [20], Sunflower [21], Jojoba [22], Sesame [23], Celery [24], Parsley [2], Almond [26], and Pistachio [27], have been extracted more efficiently utilizing SFE.

This study investigated the employment of supercritical CO_2 to recover oil from hibiscus flowers. Furthermore, Gas Chromatography-Mass Spectrometry (GC-MS) was implemented to analyze the chemical composition of the extracted oil under ideal conditions. Response surface analysis was also used to determine how SFE operating conditions affected output quality [28].

II. MATERIALS AND METHODS

A. Materials

The hibiscus flowers were acquired from a natural flower shop supplied by Nature Flower Enterprise. The flowers were baked at 75°C for 1 hour to dry. The crushing of dried flowers increased the available contact area. 80 g of flowers were washed in water to remove contaminants.

B. Instrumentation

This study used a Retsch Ultra Centrifugal Mill ZM 200 grinder, a hot air-drying oven (Thermo Scientific Heracus), an SFE system by Separex (Champigneulles, France), an experimental plan, and a GC-MS (Agilent 5975C inert, USA) analyzer.

C. Supercritical CO_2 Extraction

The Separex 4219 extraction unit (Separex, France) was utilized to perform the steps required for SFE. This tool is compatible with 5.0, 10.5, and 20.0 cm^3 autoclave breaking points (Axes). 5.0 cm of autoclave breaking points were put into service in this investigation. Hibiscus bloom powder of a known mass was weighed and measured, the reactor's pressure and temperature were adjusted, and the autoclave was stacked. The reactor was allowed to cool down after the oil was extracted.

D. Experimental Design

The yield (Y) and properties of the essential oil extracted from Hibiscus flowers with supercritical CO_2 depend on the pressure and temperature used to extract the oil. Employing a 32-central composite design from response surface analysis, the best SFE factors for getting oil from hibiscus flowers were found. Table I displays the results of an analysis of the extraction yield as a function of two independent variables: pressure (100-300 bar, A) and temperature (300-350 K, B). The experimental matrix (Table I), ANOVA analysis, regression coefficient calculation, and data visualization were all carried out in Design Expert 7.1.6 with a response surface plot and a contour plot. Equation (1), a second-order response surface model, was applied to figure out the results of the experiments. Comparing the predicted and obtained values shows how well the model worked.

$$Y = a_0 + \sum_{i=1}^{2} a_i A_i + \sum_{j=1}^{2} a_j B_j + \sum_{i=1}^{2} \sum_{j=1}^{2} a_{ij} A_i B_j + \sum_{i=1}^{2} a_{ii} A^2{}_i + \sum_{j=1}^{2} a_{jj} B^2{}_j + \sum_{i=1}^{2} \sum_{j=1}^{2} a_{ij} A^2{}_i B_j + \sum_{i=1}^{2} \sum_{j=1}^{2} a_{ij} A_i B^2{}_j \qquad (1)$$

where Y refers to the response for variables, and a_0, a_i, a_{ii}, a_{ij}, and a_{jj} are consistent coefficients of the object, direct, quadratic, and intelligent terms, respectively. A_i and B_j are the autonomous factors of pressure and temperature, accordingly.

TABLE I. FACTORS AND STANDARDS EXAMINED FOR THE EXPLORATORY OUTLINE (RSM)

Symbol	Independent variables	Coded levels		
		Low (-1)	Middle (0)	High (+1)
A	Pressure (bar)	100	200	300
B	Temperature (K)	300	325	350

E. GC-MS Analysis

The Agilent 5975C series GC-MS was implemented to analyze the oil's chemical composition, which is made of 100% dimethylpolysiloxane and DB-WAX (30 m, 0.25 mm, ID 2.5 m) under ideal SFE conditions. Starting at 60°C, the working temperature increased at a rate of 20°C/min to a peak of 250°C, where it was maintained for 10 minutes. A speed of 30 cm/s for the helium gas was utilized. The oils extracted at 200 bar and 325 K, as well as at 200 bar and 300 K, were compared. To determine what chemicals they were, the National Institute of Standards and Technology (NIST) library was consulted. Mass spectral data obtained from oil and pure standards injected under identical conditions allowed differentiation of the compositions.

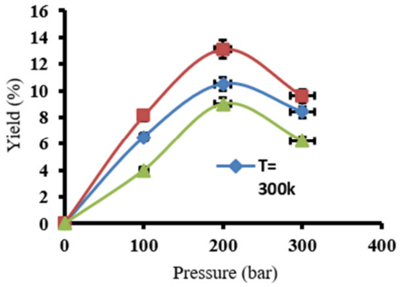

Fig. 1. The yield for oil at various pressures and temperatures.

III. RESULTS AND DISCUSSION

A. Supercritical CO_2 Extraction

The influences of pressure and temperature on the supercritical CO_2 extraction yield were analyzed and Table II summarizes the results of the various experimental iterations. Both pressure and temperature affected oil production. Oil production changed significantly when the pressure increased from 100 to 200 bar. At 200 bar, oil production was at its highest level. However, after 200 bar, the oil production began to decrease. As pressure increases, the supercritical liquid's thickness increases, making it difficult to dissolve [29]. One possible explanation for the decrease in yield above 200 bar is that higher pressure can sometimes make the solute less soluble, allowing liquid particles to move more quickly into the solid pores. The solute is thus dissociated. As more pressure is put on the substantial grid-free space, the extraction yield may also change. In this example, the product increased by increasing the temperature from 300 to 325 K. At temperatures higher than 325 K, oil production decreased [30]. However, the oil yield was almost temperature-free at 100 bars. The wide range of possible temperature changes affects the oil yield, as a rise in temperature can dissolve solids more easily in supercritical liquids [30]. Solubility in oil is controlled by the equilibrium between the vapor pressure of the solute and the dissolvable consistency [31].

TABLE II. THE YIELD OF HIBISCUS OIL EXTRACTION (% OIL EXTRACTED/80 G DRY FLOWER)

Run	Pressure (bar)	Temperature (K)	Observed yield (%)
1	100	300	6.5
2	100	350	4.1
3	100	325	8.1
4	200	325	13.11
5	200	300	10.5
6	200	350	9.1
7	300	300	8.4
8	300	325	9.6
9	300	350	6.2

B. *Hibiscus Flower Oil Extracted Characterization*

Table III lists several chemicals, including methyl palmitate, decanoic acid ethyl ester, 7-formylbicyclo[4.1.0] heptanes, (Z)-9-pentadecadien-1-ol, 2-methyl-propanamide, and 1-(2-adamantylidene) semicarbazide. Hibiscus blossom oil also contained a large amount of aliphatic aldehyde and vegetable hydrocarbons. This made the 40% oil content and the total mass at 200 bar of pressure abundantly clear. Potential causes include the impact of factors, such as altitude, precipitation, and temperature on oil production.

TABLE III. MAJOR COMPOSITIONS IN THE HIBISCUS FLOWER OIL EXTRACTED

RT (min)	Compounds	Composition at 200 bar, 300 K (%)	Composition at 200 bar, 325 K (%)	Composition at 300 bar, 350 K (%)
39.672	Methyl palmitate	9.52	12.70	10.74
41.843	Decanoic acid, ethyl ester	55.32	57.31	53.43
44.544	7-Formylbicyclo[4.1.0]heptanes	8.87	6.79	4.68
44.635	(Z)6,(Z)9-Pentadecadien-1-ol	22.61	25.91	27.29
44.849	Propanamide, 2-methyl-	11.54	9.99	10.11
55.349	1-(2-Adamantylidene) semicarbazide	4.69	5.21	7.55

RT: Retention Time

C. *Response Surface Analysis*

The results disclosed that hibiscus blossom oil yield ranged from 4.11 to 13.11%. This demonstrates the significance of pressure and temperature in determining the oil yield. ANOVA was used to earn a second-degree equation:

$$Y = +12.09 + 1.16 * A - 1.52 * B + 0.35 * A * B - 3.52 * A^2 - 1.01 * B^2 - 0.238 * A^2 * B + 0.034 * A * B^2 \qquad (2)$$

The fit of the model was quite satisfactory, as indicated by the multiple correlation coefficient R^2 value of 0.9986. Table IV portrays the nine experiments and their observed and predicted results. Most points are clustered around the first bisector line, confirming that the experimental and predicted data agree. The quality of the model was assessed in terms of Fisher's Exact Test via the ANOVA F-test. To do this, the F-value, the ratio between the square of the model's mean, and the sum of the residual error were employed. There is statistical significance in the model, as the F-value is 503.68. Table IV exhibits that the model's p-value is less than 0.05, indicating that it is statistically significant. The effects of pressure (A), heat (B), two-tier relationships between the two (AB), pressure (A^2), and heat (B^2) were all relatively significant. The fact that many other terms had values higher than 0.1000 indicates that the model terms could be more helpful. In terms of oil production, the hibiscus flower was most sensitive to pressure's immediate effect (A). Since pressure is polar, it can dynamically interact with temperature. This result agrees with the results of [32]. The positioning of the crucial components was determined by the predicted F-value. Therefore, in this study, the following is the order of importance for the features: When comparing similar sets of numbers, $A^2 > B > B^2 > A > AB > A^2B > AB^2$. Furthermore, the p-value for the lack of fit is only 3.49%. R^2 is used to determine whether a relapse is the right move. The determined R^2-value was 0.9986, which is close to 1 and is therefore acceptable. There was some ambiguity between the reported R^2 of 0.9349 and the adjusted R^2 of 0.9966. A ratio greater than 4 is preferable. In this case, the estimation was significantly higher than 4, with a balance of 60.510, revealing a superb indication.

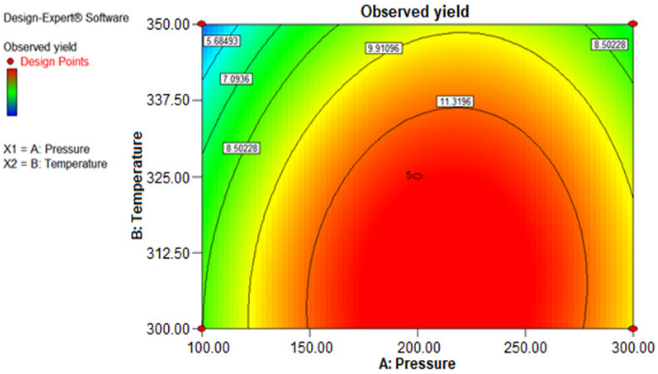

Fig. 2. Optimum yield for oil extraction.

D. *Optimum Conditions*

Response surface analysis was implemented to determine how changes in extraction parameters affect the amount of oil that can be extracted from hibiscus blooms. The highest oil yield, 13.11%, was achieved at a pressure (A) of 200 bar and a temperature (B) of 325 K. Figure 2 depicts the three-dimensional response surface discovered by analyzing the optimal pressure and temperature for oil production. At first, the oil yield increased but then decreased as the temperature rose at all three pressures (100, 200, and 300 bar). The experiments showed that the amount of oil extracted from Hibiscus flowers depends on how much pressure will be applied and how hot it is.

IV. CONCLUSION

This study investigated the use of supercritical CO_2 to extract oil from hibiscus blooms. This innovative approach highlights the way pressure directly affects the quantity of oil extracted, while the temperature of the extraction environment impacts the oil's quality. Through the application of response surface analysis, this study successfully identified the optimal values for pressure and temperature during the SFE process. Under these optimal conditions, the extraction of oil from hibiscus flowers revealed the presence of six distinct compounds, highlighting the technique's efficiency and specificity. At 325 K and 200 bar, the oil yield was maximized at 13.11% per 80 g of dry flower, indicating that the hibiscus flower, when processed with SFE, produces a substantial amount of oil. The novelty of this study lies in its approach to optimizing the SFE conditions, and its contribution extends to demonstrating the potential of hibiscus flowers as a source of valuable oil, utilizing supercritical CO_2 for efficient and environmentally friendly extraction.

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