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XUAN-TIEN LE[1,2]
https://orcid.org/0000-0003-2762-8925
THAI-HUNG VO[1,2]
https://orcid.org/0009-0001-6328-2151
THANH NGOC NGUYEN[3,4]
https://orcid.org/0000-0002-9333-9569
MINH-CHAU PHAM-VU[1,2]
https://orcid.org/0009-0008-5537-4938

[1]Department of Chemical Engineering, Ho Chi Minh University of Technology (HCMUT), Ho Chi Minh City, Vietnam
[2]Vietnam National University Ho Chi Minh City (VNU-HCM), Ho Chi Minh City, Vietnam
[3]NTT Hi-Tech Institute, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam
[4]Nguyen Tat Thanh University, Center for Hi-Tech Development, Saigon Hi-Tech Park, Ho Chi Minh City, Vietnam

SCIENTIFIC PAPER

UDC

FRACTIONAL DISTILLATION OF GERANIOL FROM *Cymbopogon martinii* ESSENTIAL OIL

Highlights

- Vacuum fractional distillation was employed to isolate geraniol from palmarosa oil
- Distillation performance was enhanced by optimizing packing type, column height, and pressure
- The combined content of geraniol and geranyl acetate reached 93.67%
- Residual geranyl acetate in the fraction contributed to a more desirable aroma profile

Abstract

Vacuum fractional distillation was applied to isolate geraniol from raw Cymbopogon martinii essential oil. Due to the close boiling points of geraniol and geranyl acetate under reduced pressure, complete separation of geranyl acetate was not achievable. However, the presence of geranyl acetate did not diminish the value of the fractionated oil owing to its pleasant aroma. To optimize the distillation process, three key parameters - packing type, column height, and operating pressure - were systematically investigated. The obtained fractions were evaluated based on yield, purity, recovery, and GC-MS analysis. Under optimal conditions, geraniol content reached 71.35% with a recovery rate of 71.50%, while the combined content of geraniol and geranyl acetate attained 93.67%. This study provided valuable insights into optimizing vacuum fractional distillation for isolating geraniol-rich fractions from palmarosa essential oil, improving product quality while minimizing thermal degradation. The findings contribute to the advancement of extraction technologies for bioactive compounds, with potential applications in pharmaceutical, cosmetic, and aromatherapy industries.

Keywords: geraniol, vacuum fractional distillation, palmarosa essential oil, Cymbopogon martinii.

INTRODUCTION

Cymbopogon martinii (palmarosa) is a species belonging to the Poaceae family, widely distributed across tropical and subtropical regions [1]. The essential oil extracted from palmarosa is extensively utilized in cosmetics, perfumery, and pharmaceuticals due to its mild fragrance and high content of geraniol, a monoterpenoid characterized by a rose-like aroma and notable biological activities, including antibacterial, anti-inflammatory, and antioxidant effects [2,3].

Correspondence: X.-T. Le, Department of Chemical Engineering, Ho Chi Minh University of Technology (HCMUT), Ho Chi Minh City, Vietnam; Vietnam National University Ho Chi Minh City (VNU-HCM), Ho Chi Minh City, Vietnam.
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Geraniol serves not only as a fragrance agent in cosmetics, perfumes, and food products but also exhibits superior mosquito-repellent efficacy compared to citronella essential oil and other common compounds such as linalool [4]. Additionally, palmarosa essential oil has been reported as an environmentally friendly bioherbicide [5] and to exhibit antibacterial activity against pathogens such as *Aggregatibacter actinomycetemcomitans*, a causative agent of periodontal disease [3]. While geraniol offers various functional benefits, it may induce skin irritation due to its propensity to undergo autoxidation, forming sensitizing compounds such as hydroperoxides, geranial, and neral [6, 7]. Notably, the allergenic potential is mainly attributed to these oxidation products rather than geraniol itself [7]. Nevertheless, geraniol remains widely used in cosmetic and fragrance applications and is included in the list of fragrance allergens requiring labeling under European Union cosmetic regulations [6,8].

Geraniol-containing essential oils are currently produced using various methods, ranging from traditional techniques such as steam distillation [8] and solvent extraction [10] to more advanced technologies including supercritical CO_2 extraction [11] and microwave-assisted extraction [12]. Although these techniques allow the recovery of essential oils with considerable geraniol content, in-depth studies on the direct separation and enrichment of high-purity geraniol from essential oils remain limited.

In our previous work on separating citronellal from Java citronella oil via fractional distillation, we unexpectedly obtained a fraction containing up to 40% geraniol from an essential oil that initially contained only 17% geraniol [13]. In addition, a simulation of citronellol - geraniol separation by vacuum distillation using Aspen Plus to evaluate the separation behavior of these constituents [14]. These findings indicate that geraniol can indeed be separated and enriched under appropriate distillation conditions, thereby offering a promising basis for developing an efficient process for obtaining high-purity geraniol for industrial applications.

To overcome the aforementioned limitations and build upon the evidence that geraniol can be enriched through distillation, this study employs vacuum fractional distillation. Operating under reduced pressure helps lower the boiling points of the components, minimize thermal degradation, and improve the separation of compounds with closely similar boiling points, such as geraniol and geranyl acetate [15]. As a result, this technique significantly enhances both the purity and recovery of geraniol while preserving its biological properties and natural aroma [13,16].

In this study, we focus on evaluating the influence of key operational parameters, including packing material, column height, and vacuum pressure, on the fractional distillation performance of palmarosa essential oil. A one-factor-at-a-time (OFAT) approach was employed, in which each variable was varied independently while maintaining the remaining parameters constant. The primary objective is to determine the optimal conditions that maximize distillation efficiency, purity, and recovery of bioactive constituents such as geraniol and geranyl acetate. The findings aim to provide a scientific and technical foundation for the effective application of vacuum fractional distillation in the production of high-quality essential oils for pharmaceutical and cosmetic industries.

MATERIALS AND METHODS

Chemicals

Palmarosa essential oil, supplied by Notessen Company Limited, Vietnam, was used as the raw material for fractional distillation. The essential oil was obtained by steam distillation of *C. martinii* leaves, as reported by the supplier, and used without further purification. Prior to distillation, residual water in the essential oil was removed using anhydrous sodium sulfate (Xilong, China). Acetone was used as the solvent for gas chromatography-mass spectrometry (GC-MS) analysis.

Equipments

A Lauda Ecoline R215 Staredition chiller (Lauda Dr. R. Wobser GMBH & Co. KG, Germany) and an Edward RV5F vacuum pump (BOC Edwards, UK) were employed for the fractional distillation process. The GC-MS analysis was conducted using a G1530A analyzer and an Agilent 5973N MSD mass spectrometer (USA). A Hermle Z206A centrifuge (Wehingen, Germany) was also used during sample preparation.

Essential oil fractionation procedure

The fractional distillation system used in this study is illustrated in Fig. 1. Each experiment was conducted using 100 g of palmarosa essential oil, which was charged into a two-neck round-bottom flask (B) equipped with a magnetic stirrer bar. The flask was heated using a heater (C) through an oil bath (D) to ensure stable and precise temperature control. The liquid temperature was monitored using a bottom thermal sensor (E). The system was equipped with a Hempel column (F) packed with random packing materials to enhance vapor-liquid contact and improve separation efficiency, while the vapor temperature at the top of the column (H) was monitored to track the distillation profile.

The vapor stream was condensed using a condenser (K) connected to a chiller system (Q) maintained at 5 °C, and the condensate was directed to a cow adapter (M) for sequential collection of fractions (A) without interrupting the process. A vacuum system comprising a vacuum pump (O), pressure controller (P), and vapor trap (N) was employed to maintain reduced pressure. All temperature sensors were integrated into a data acquisition system (I) connected to a computer (J), enabling real-time monitoring and recording of temperature profiles throughout the distillation process.

Fractions were collected based on characteristic changes in the temperature profile monitored at the top of the column. The initial fraction (F1) was collected within the low-temperature range (38-42 °C). Following a sharp increase in temperature to approximately 150 °C, the collection was switched to the main fraction (F2). The remaining liquid in the flask after distillation was designated as the bottom fraction (B). These temperature ranges were defined according to the observed distillation profile (Section 3).

Based on the defined fractionation criteria, the effects of key operating parameters, including packing type (helice, wire mesh, and spiral), column height (100, 200, 300, 400, and 500 mm), and operating pressure (80, 60, 40, and 20 mmHg), were systematically investigated using a one-factor-at-a-time approach. The optimization was carried out sequentially, starting with packing type at fixed conditions, followed by column height and operating pressure.

Identification and analysis of essential oil components

The essential oil sample was diluted to 1000 ppm in acetone, and 1 µL was injected into a GC-MS system consisting of an Agilent 7820A gas chromatograph coupled with an Agilent 5977E mass spectrometer. Gas chromatographic separation was performed on an HP-5MS column

(30 m × 0.25 mm i.d. × 0.25 μm film thickness) using helium as the carrier gas at a flow rate of 1 mL/min. The injector temperature was set at 250 °C with a split ratio of 1:50. The oven temperature program started at 60 °C and was held for 2 min, then increased at 30 °C/min to 147 °C, followed by a slower ramp of 0.25 °C/min to 149 °C, and finally increased at 20 °C/min to 250 °C and held for 10 min. Mass spectrometric detection was carried out in scan mode with an ionization energy of 70 eV, a scan rate of 1 scan/s, and an ion source temperature of 220 °C.

The chemical constituents were identified by comparing their mass spectra with those in the NIST library (version 2.0a). In addition, geraniol and geranyl acetate were confirmed by comparison with authentic standards analyzed under the same GC-MS conditions.

Evaluation of distillation performance

The distillation performance was evaluated in terms of yield and recovery. The chemical composition of each fraction was determined by GC-MS and reported as peak area percentages, which were used for recovery calculation. The yield of each fraction was expressed as a percentage using Eq. (1).

$$\text{Yield} = \frac{w_F}{w_{Raw}} \times 100 \qquad (1)$$

where w_F is the mass of the fraction, and w_{Raw} is the mass of the raw material (100 g). The recovery percentage was calculated using Eq. (2):

$$\text{Recovery} = \text{Yield} \times \frac{w_x}{w_{x,Raw}} \times 100 \qquad (2)$$

where w_x is the peak area percentage of component x in the obtained fraction, and $w_{x,Raw}$ is the corresponding peak area percentage in the raw material.

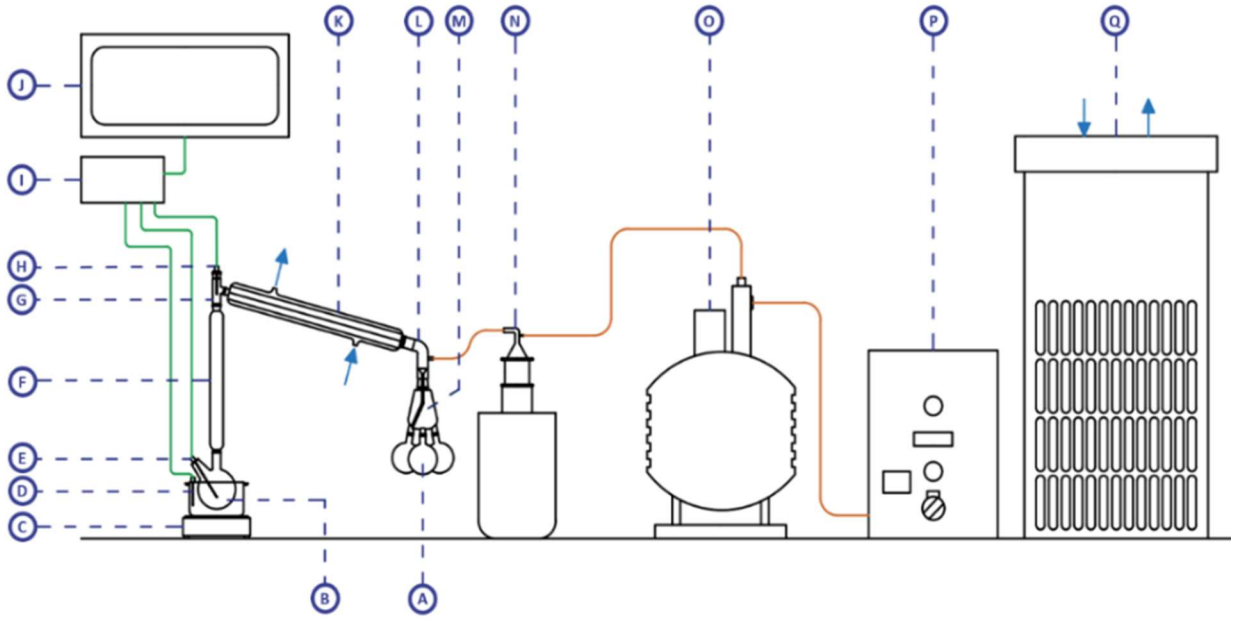

Figure 1. Palmarosa essential oil fractional distillation system (A): Product flasks; (B): Two-neck flask; (C): Heater; (D): Oil bath; (E): Bottom thermal sensor; (F) Hampel distillation column; (G): Three-way distillation adapter; (H): Top-column thermal sensor; (I): Thermal transceiver station; (J): Computer; (K): Condenser; (L): Vacuum take-off adapter; (M): Cow adapter; (N): Vapor trap; (O): Vacuum pump; (P): Pressure controller; (Q): Chiller.

All distillation experiments were carried out in triplicate. The obtained data are expressed as mean ± standard deviation, and differences among operating conditions were assessed by one-way analysis of variance (ANOVA). Statistical significance was established at $p < 0.05$.

RESULTS AND DISCUSSION

Fractional distillation of geraniol from *C. martinii* essential oil: Raw material and fraction characterization

Chemical composition of raw palmarosa essential oil

C. martinii essential oil was obtained by steam distillation of leaves collected in May from northern Vietnam at the full flowering stage, characterized by brown inflorescences. GC-MS analysis showed that the geraniol content (61.65%) was lower than that reported in the literature (70%), whereas the geranyl acetate content (24.27%) was higher than the value reported for this compound (15%) [17] (Table 1). These variations in composition may be attributed to differences in growth conditions, harvesting time, and extraction procedures.

Based on the compositional data in Table 1, the fraction containing predominantly geraniol and geranyl acetate would account for the largest proportion of the distilled product, exceeding 85%. In principle, low-boiling compounds would be collected in the initial fraction, whereas the main fraction would be enriched in β-citral, geraniol, geranial, and geranyl acetate before the system approaches the boiling range of higher-boiling compounds such as β-caryophyllene. However, under vacuum distillation at 60 mmHg, the reduced pressure lowers the boiling points of these components and narrows the temperature differences between them, particularly between geraniol and geranyl acetate, thereby promoting co-distillation within the same fraction [18].

Table 1. Chemical composition of raw palmarosa essential oil.

Compound	*Retention time*, min	*Retention index*, min	*Peak area*, %A	*Boiling point at 760 mmHg*, °C	*Predicted boiling point at 60 mmHg*, °C
Isopropyl-n-propionate	4.46	905	0.31	108	33.8
Limonene	6.06	991	0.05	176	94.0
γ-terpinene	6.16	996	0.45	183	100.2
Linalool	6.64	1028	1.19	198	113.4
Cresol	7.79	1071	0.77	202	117.0
β-Citral	8.31	1087	0.57	229	140.8
Geraniol	8.42	1099	61.65	229	140.8
Geranial	8.72	1112	1.20	229	140.8
Geranyl acetate	10.84	1170	24.27	240	150.6
β-Caryophyllene	12.47	1274	0.16	262	170.0
Geranyl isobutyrate	17.28	1455	2.96	295	199.2
β-Caryophyllene oxide	18.44	1495	0.24	301	204.5

Temperature behavior during vacuum fractional distillation

Fractional distillation of *C. martinii* essential oil was performed to complement the GC-MS analysis of its raw composition. The distillation was conducted using 100 g of raw oil in a system equipped with a 200 mm Hempel column packed with Helice packing (2 mm inner diameter and 10 mm length) and operated under vacuum at 60 mmHg. During the distillation, the temperatures of both the top vapor and the bottom liquid were recorded every second, providing a detailed temperature profile (Fig. 2A).

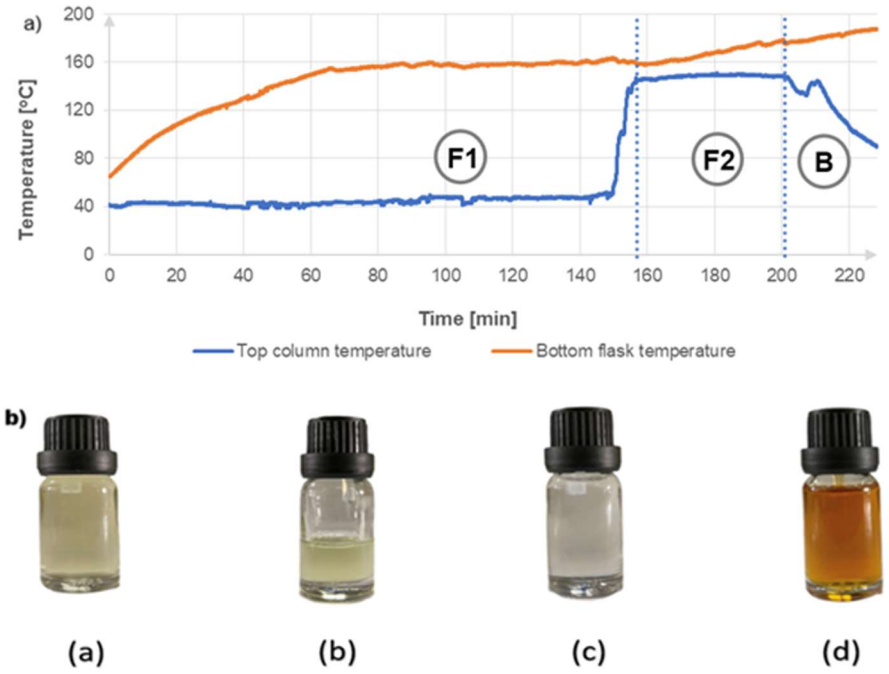

Figure 2. Temperature profile (A) and fraction appearance (B) during palmarosa oil distillation using a 200 mm Hempel column with Helice packing at 60 mmHg:(a) raw palmarosa essential oil, (b) first fraction (F1), (c) second fraction (F2); and (d) bottom fraction (B).

As shown in Fig. 2A, during the distillation process, the vapor temperature at the top of the column initially remained stable at 38-42 °C, corresponding to the separation of the more volatile components in the first fraction (F1). After approximately 150 minutes, the vapor temperature increased sharply to 148-154 °C, indicating the transition to the main fraction (F2), which contained the less volatile major constituents of the oil. These distinct temperature regions provided a practical basis for fraction collection during the distillation process.

The collected fractions, namely F1, F2, and B, exhibited noticeable differences in volume, color, and aroma (Fig. 2B), reflecting differences in their chemical composition. Fraction F2 was obtained in the largest amount and showed a characteristic rose-like aroma, consistent with its enrichment in geraniol and geranyl acetate. In contrast, F1 exhibited a fresher, greener odor, whereas the bottom fraction (B) showed a darker reddish-brown appearance and a more pungent odor, suggesting the accumulation of less volatile and possibly thermally affected components. These observations further support the effectiveness of fractional distillation in separating palmarosa essential oil into fractions with distinct physicochemical characteristics.

GC-MS composition, yield, and recovery of distillation fractions

As shown in Table 2, the main fraction (F2) exhibited a composition broadly similar to that of the raw essential oil, with geraniol increasing from 61.65% to 65.88% and geranyl acetate remaining nearly unchanged (24.27% vs. 24.11%). In contrast, fraction F1 showed a marked increase in linalool content, while fraction B retained a relatively high proportion of geranyl acetate despite its much lower geraniol content. These results indicate that fractional distillation enabled a partial enrichment of the major oxygenated constituents in F2 while redistributing other components into F1 and B, rather than achieving effective separation of geraniol and geranyl acetate.

The main fraction (F2) exhibited a substantially higher yield than the other fractions, accounting for 68.5% of the distillate (Table 3). Nevertheless, this value was lower than the proportion theoretically expected from the compositional data of the raw oil, in which geraniol and geranyl acetate together accounted for more than 85%. This discrepancy may be attributed to oil retention on the packing material, incomplete separation between adjacent fractions, and material losses during distillation. The recovery data further support the limited separation performance, as F2 showed the highest recovery of both compounds, whereas fractions F1 and B still retained a portion of the target constituents. The retention of both geraniol and geranyl acetate in fraction B indicates incomplete separation under the selected vacuum distillation condition. This behavior is understandable because a certain liquid holdup must remain in the distillation flask to sustain continuous vapor generation and vapor–liquid mass transfer through the column. As distillation proceeds and the liquid volume in the flask gradually decreases, vapor generation becomes progressively less effective, thereby reducing the upward transport of the remaining components and limiting their further separation and recovery in the distillate [13]. Consequently, the bottom fraction ultimately accounted for 24.5% of the initial feed.

The fractionation of geraniol and geranyl acetate under reduced pressure was governed by their relative volatility and by vapour - liquid mass transfer within the column. Only a slight compositional change was observed in the main fraction, with a limited increase in geraniol and little change in geranyl acetate. This behavior indicates that, under vacuum conditions, the volatility difference between these two major components was insufficient to permit effective fractionation.

Table 2. GC-MS composition of palmarosa essential oil and the resulting fractions.

	Geraniol (%)	*Geranyl acetate* (%)	*Geraniol and geranyl acetate* (%)	*Hydrocarbon terpenes* (%)	Linalool (%)
Raw material	61.65	24.27	85.92	0.50	1.19
Fraction F1	54.43	11.66	66.09	0.46	18.73
Fraction F2	65.88	24.11	89.99	1.94	1.41
Fraction B	14.80	28.20	43.00	0.86	0.35

Table 3. Distillation fractions yield and recovery of geraniol and geranyl acetate.

Fraction	Yield (%)	*Recovery (%)*		
		Geraniol (%)	*Geranyl acetate* (%)	*Geraniol and geranyl acetate* (%)
F1	1.5	1.28	0.70	1.12
F2	68.5	73.15	67.99	71.69
B	24.5	5.88	28.48	12.27

As shown in Table 1, the predicted boiling points of geraniol and geranyl acetate at 60 mmHg were 140.8 and 150.6 °C, respectively, corresponding to a difference of less than 10 °C, which favored co-distillation and limited the selectivity of the process. In addition, the absence of controlled top reflux in the present system likely restricted phase contact inside the column, thereby further reducing the separation efficiency for compounds with closely similar volatilities [19]. Overall, vacuum fractional distillation was effective for obtaining a geraniol-enriched fraction with improved product quality; however, the process should be regarded as partial enrichment rather than complete separation of geraniol and geranyl acetate.

Influence of operating parameters on the fractional distillation of *C. martinii* essential oil

Following the initial characterization of the essential oil fractions, the effects of key operating parameters, including packing type, column height, and vacuum pressure, on the performance of vacuum fractional distillation were further investigated. These factors were systematically evaluated based on temperature profiles, component distribution, fraction yield, and recovery of the target compounds.

Effect of packing type

Packing materials significantly affect the separation efficiency in vacuum fractional distillation by influencing heat transfer and mass exchange within the column. Various properties of the packing, including size, shape, and porosity, play important roles in optimizing the separation of components with close boiling points [20,21]. Building on this understanding, the study evaluated three types of packing materials used in a 200 mm Hempel column operating under 60 mmHg vacuum pressure.

The temperature profile analysis presented in Fig. 3A demonstrated that packing type markedly influenced vapor flow behavior and thermal stability during vacuum fractional distillation. Among the tested packings, helice produced the most stable F2 temperature profile, whereas spiral packing showed the greatest fluctuation. Owing to its high porosity (0.98), helice packing promoted a more continuous vapor flow through the column and resulted in shorter retention times. In contrast, spiral packing, with a lower porosity (0.85), caused more intermittent vapor transport and longer retention times, leading to prolonged retention of the F2 fraction. Wire mesh packing, with an intermediate porosity of 0.94, exhibited behavior between these two extremes, providing a relatively stable temperature profile with moderate retention time.

These observations indicate that packing structure strongly affected the hydrodynamic conditions inside the column and, consequently, the distillation behavior. While the highly porous helice packing favored smoother vapor movement, it may also have reduced vapor-liquid contact and limited mass transfer efficiency. By contrast, the lower porosity of spiral packing increased resistance to vapor passage and extended residence time. Wire mesh packing provided a more balanced performance, combining acceptable thermal stability with sufficient vapor-liquid interaction. For this reason, it was considered the most suitable packing for subsequent experiments.

GC-MS results in Table 4 further showed that packing type affected the composition of fraction F2. As packing porosity decreased, the geraniol content increased from 65.88% for helice packing to 70.57% for wire mesh and 72.03% for spiral packing, whereas geranyl acetate showed a decreasing trend. This result suggests that lower-porosity packing improved fractionation efficiency to some extent by prolonging vapor residence time and enhancing separation between compounds with slightly different volatilities. However, the increase in geraniol concentration was relatively limited, which may be attributed to the already high initial concentrations of both geraniol and geranyl acetate in the raw material, together with the narrow boiling point difference between them.

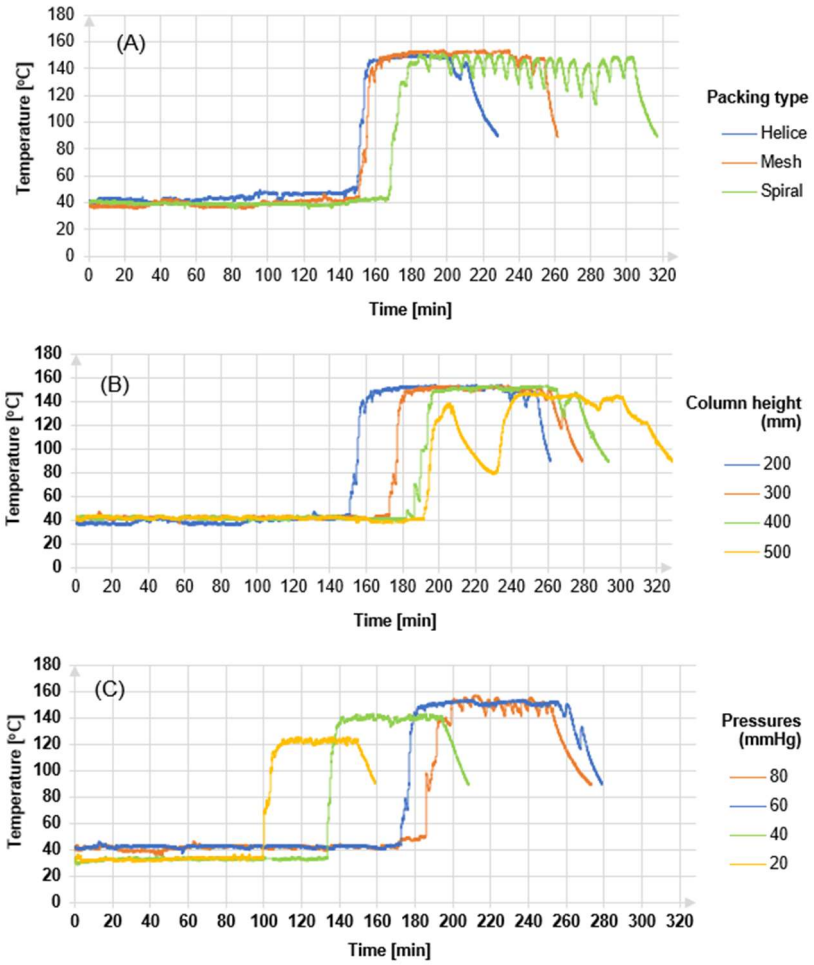

Figure 3. Top-column temperature profiles during vacuum fractional distillation: (A) Comparison of packing types; (B) Effect of column height (200, 300, 400, and 500 mm); and (C) Effect of operating pressure (80, 60, 40, and 20 mmHg).

Table 4. Influence of distillation parameters on the composition of fraction F2.

	Geraniol (%)	*Geranyl acetate* (%)	*Geraniol and geranyl acetate* (%)
Packing type			
Helice	65.88	24.11	89.99
Mesh	70.57	22.23	92.77
Spiral	72.03	20.94	92.97
Column height			
200 mm	70.54	22.23	92.77
300 mm	71.35	22.32	93.67
400 mm	71.55	21.37	92.92
500 mm	72.32	16.76	89.07
Operating pressure			
80 mmHg	73.97	24.27	94.59
60 mmHg	71.35	22.32	93.67
40 mmHg	67.81	26.24	91.05
20 mmHg	65.06	26.56	91.63

The influence of packing type on fraction yield is presented in Fig. 4. No significant difference was observed for fraction F1, whereas clear differences were found for fractions F2 and B. Spiral packing gave the lowest F2 yield (51.5%), while helice and wire mesh resulted in higher values. This trend can be explained by the lower porosity and higher specific surface area of spiral packing, which increased resistance to vapor flow and promoted liquid hold-up within the column, thereby reducing the amount of condensate collected in F2 and increasing the proportion remaining in the bottom fraction B [22].

Fig. 4 also shows that recovery was strongly influenced by fraction yield. Although spiral packing produced the highest geraniol concentration in fraction F2, its geraniol recovery (60.12%) was lower than that of helice and wire mesh packings. A similar trend was observed for geranyl acetate, with spiral packing giving the lowest recovery (44.38%) among the three packing types. These results indicate that lower porosity improved the compositional enrichment of geraniol in F2, but at the expense of fraction yield and overall recovery. In contrast, helice packing gave higher recovery but weaker fractionation performance, likely because its high porosity reduced the extent of vapor-liquid interaction. Overall, wire mesh packing provided the most favorable balance between compositional improvement and recovery of the target compounds, and was therefore selected for the subsequent experiments.

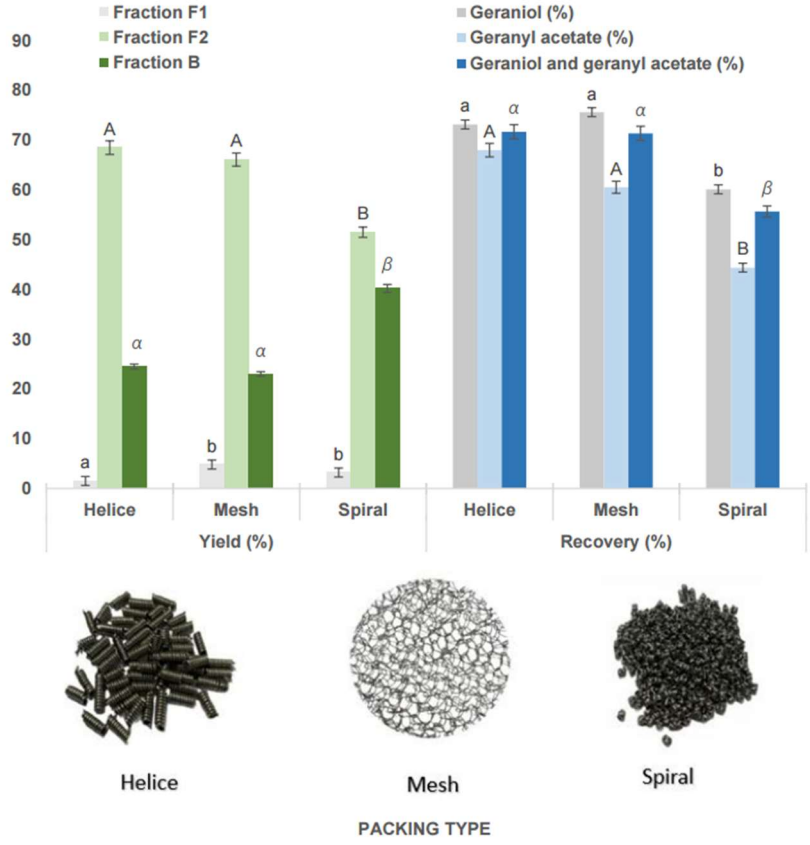

Figure 4. Effect of packing type on fraction yields and on the recovery of geraniol and geranyl acetate in fraction F2. Different lowercase, uppercase, and Greek letters indicate significant differences among the first, second, and third bar series, respectively ($p < 0.05$).

Effect of column height

Column height directly influenced the efficiency of vacuum fractional distillation, as increasing the column height generally prolonged vapor residence time and improved separation performance. However, an excessively high column could also lead to greater heat loss and reduced process stability [23]. The effect of column height on the distillation process was investigated using wire mesh packing at 60 mmHg with column heights of 100, 200, 300, 400, and 500 mm.

As shown in Fig. 3B, vapor residence time increased with increasing column height. However, the 500 mm column exhibited an unstable temperature profile, in which the F2 temperature initially increased and then declined rapidly, indicating reduced process stability, most likely due to significant heat loss along the extended vapor path. In contrast, the 100 mm column showed severe vapor surging, which necessitated termination of the experiment. Therefore, subsequent experiments were conducted only with column heights ranging from 200 to 500 mm.

Table 4 further demonstrates that column height had a modest effect on the composition of fraction F2. As the column height increased from 200 to 500 mm, the geraniol content increased from 70.54% to 72.32%, whereas geranyl acetate decreased from 22.23% to 16.76%. However, the highest combined content of geraniol and geranyl acetate was obtained at 300 mm (93.67%), while the lowest value was observed at 500 mm (89.07%). This trend can be attributed to the greater packing bed height and interfacial contact area at longer columns, which effectively increased the number of theoretical plates and enhanced fractionation efficiency [24]. Under these conditions, the slightly higher boiling point of geranyl acetate relative to geraniol under selected vacuum conditions (150.6 °C vs. 140.8 °C) made its transfer into the main fraction less favorable as separation became more effective. Consequently, although increasing column height slightly enriched geraniol in fraction F2, it also promoted greater retention of geranyl acetate in the bottom fraction, thereby reducing the combined enrichment of the two target constituents in the main fraction. These findings indicate that increasing column height improved separation only up to a certain point, beyond which the combined enrichment of the target constituents in fraction F2 became less favorable.

The effect of column height on yield and recovery is presented in Fig. 5. The yield of fraction F2 decreased markedly with increasing column height, from 66.1% at 200 mm to 23.1% at 500 mm, whereas the yield of the bottom fraction increased from 23.0% to 64.7%. A similar trend was observed for recovery. Although the highest geraniol content in F2 was obtained at 500 mm, its recovery was the lowest (27.04%) because of the sharp decline in F2 yield. Geranyl acetate recovery also decreased substantially with increasing column height, from 60.54% at 200 mm to 15.91% at 500 mm. These results demonstrate that improved compositional enrichment at greater column heights was achieved at the expense of fraction yield and recovery.

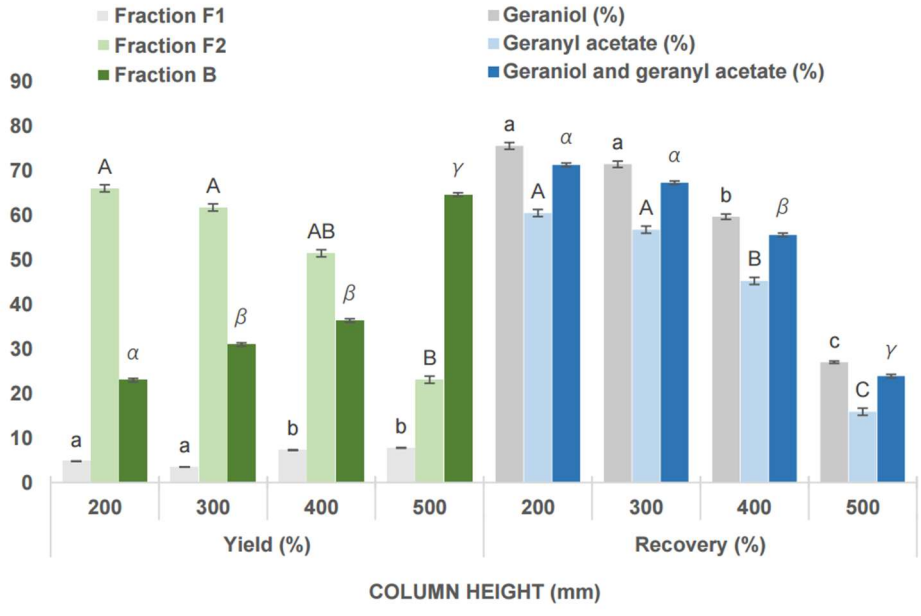

Figure 5. Effect of column height on fraction yields and on the recovery of geraniol and geranyl acetate in fraction F2. Different lowercase, uppercase, and Greek letters indicate significant differences among the first, second, and third bar series, respectively ($p < 0.05$).

Overall, a column height of 300 mm was selected for further experiments because it provided the best balance between separation performance and distillation efficiency. Under this condition, fraction F2 retained a relatively high yield (61.8%), a high combined content of geraniol and geranyl acetate (93.67%), and satisfactory recovery of the target compounds, while maintaining a more stable temperature profile than the 500 mm column and avoiding the vapor surging observed at 100 mm. To isolate the effect of operating pressure in the subsequent study, the packing type and column height were fixed at wire mesh and 300 mm, respectively.

Effect of operating pressure

The final parameter investigated in this study was operating pressure. Experiments were carried out using wire mesh packing and a 300 mm column at four pressures: 80, 60, 40, and 20 mmHg.

As shown in Fig. 3C, the F2 collection temperature was strongly affected by operating pressure and decreased as the pressure was reduced. At 60, 40, and 20 mmHg, the F2 collection temperatures were 152, 140, and 122 °C, respectively, in good agreement with values predicted by the Clausius-Clapeyron relationship [25]. In contrast, the experiment at 80 mmHg showed considerable instability, with the F2 temperature fluctuating between 140 and 158 °C. This behavior suggests less stable vapor transport at the higher pressure, making it more difficult for the F2 fraction to move consistently to the top of the column. By comparison, lower pressures facilitated smoother vapor flow and produced more stable temperature profiles.

Table 4 shows that the composition of fraction F2 changed with operating pressure. As the pressure decreased from 80 to 20 mmHg, the geraniol content declined from 73.97% to 65.06%, whereas geranyl acetate remained relatively stable. Consequently, the combined content of geraniol and geranyl acetate decreased from 94.59% to 91.63%. This trend suggests that lowering the pressure facilitated the transfer of a broader range of components into the main fraction, thereby increasing F2 yield but reducing its compositional selectivity toward geraniol.

This behavior was further reflected in the yield and recovery profiles shown in Fig. 6. As operating pressure decreased, the yield of fraction F2 increased markedly from 22.4% to 78.4%, while the yield of the bottom fraction decreased substantially. Although the geraniol content in F2 declined at lower pressures, geraniol recovery increased from 26.84% to 82.76% because a much larger proportion of the distillate was collected in the main fraction. Notably, the geraniol recovery at 40 mmHg was slightly higher than that at 20 mmHg, despite their similar F2 yields, because the geraniol content at 40 mmHg (67.81%) remained higher than at 20 mmHg (65.06%). A similar increase was observed for geranyl acetate recovery. These results indicate that pressure optimization requires balancing compositional purity with fraction yield and recovery, while also considering the risk of thermal degradation at excessively high distillation temperatures.

Overall, the F2 fraction obtained at 80 mmHg showed the highest geraniol purity but suffered from very low recovery, which limited its practical value. In contrast, the fractions obtained at 40 and 20 mmHg provided higher recovery but lower geraniol content, making them less suitable when compositional quality was prioritized.

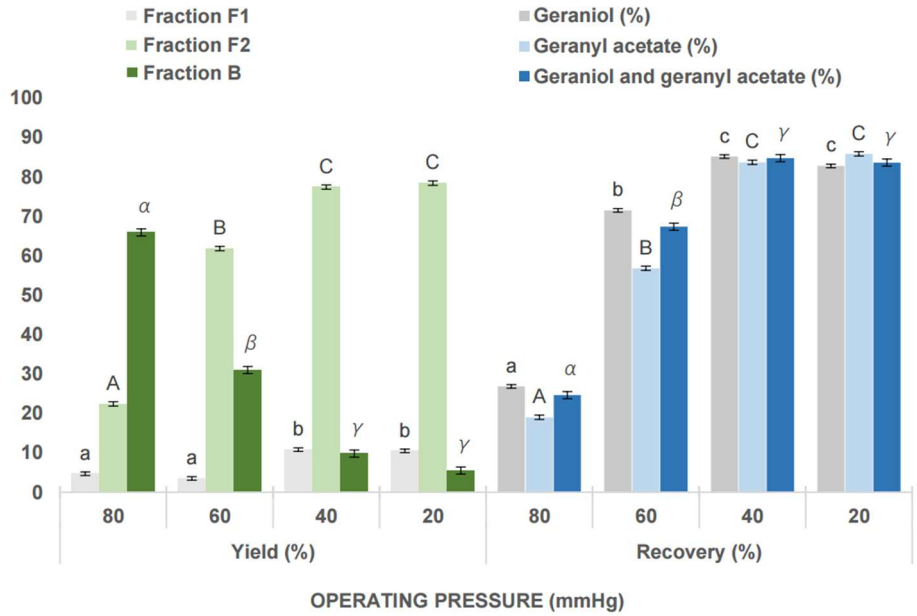

Figure 6. Effect of operating pressure on fraction yields and on the recovery of geraniol and geranyl acetate in fraction F2. Different lowercase, uppercase, and Greek letters indicate significant differences among the first, second, and third bar series, respectively ($p < 0.05$).

Considering both purity and recovery, 60 mmHg provided the most favorable overall balance. Accordingly, 60 mmHg, together with wire mesh packing and a 300 mm column, was selected as the most suitable operating condition for producing an F2 fraction intended for fragrance applications.

Under the selected operating conditions, geraniol was enriched by approximately 10%, increasing from 61.65% in the raw material to 71.35% in the main fraction, while the combined content of geraniol and geranyl acetate reached 93.67%. In addition to its improved compositional profile, the obtained fraction exhibited a more pleasant rose-like aroma, further supporting its practical value for fragrance material. Furthermore, this fraction may serve as a useful intermediate for subsequent upgrading processes, such as selective hydrolysis of geranyl acetate in the mixture to increase geraniol content, or biocatalytic acetylation of geraniol using lipase to produce geranyl acetate-rich

material [26], potentially enabling the production of highly purified geraniol or geranyl acetate.

CONCLUSION

Vacuum fractional distillation proved effective in optimizing the recovery and enhancing the quality of *C. martinii* essential oil. The study examined the effects of factors such as packing type, column height, and vacuum pressure, with optimal conditions identified as a 300 mm column, wire mesh packing, and 60 mmHg pressure. Under these conditions, the main fractions obtained contained 71.35% geraniol and 22.32% geranyl acetate. This research not only improved the composition of palmarosa essential oil but also demonstrated its potential for fragrance applications by producing geraniol-enriched fractions with enhanced aroma properties.

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XUAN-TIEN LE[1,2]

THAI-HUNG VO[1,2]

THANH NGOC NGUYEN[3,4]

MINH-CHAU PHAM-VU[1,2]

[1]Department of Chemical Engineering, Ho Chi Minh University of Technology (HCMUT), Ho Chi Minh City, Vietnam
[2]Vietnam National University Ho Chi Minh City (VNU-HCM), Ho Chi Minh City, Vietnam
[3]NTT Hi-Tech Institute, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam
[4]Nguyen Tat Thanh University, Center for Hi-Tech Development, Saigon Hi-Tech Park, Ho Chi Minh City, Vietnam

NAUČNI RAD

FRAKCIONA DESTILACIJA GERANIOLA IZ ETARSKOG ULJA *Cymbopogon martinii*

Vakuumska frakciona destilacija primenjena je za izolovanje geraniola iz sirovog etarskog ulja Cymbopogon martinii. Zbog bliskih tačaka ključanja geraniola i geranil-acetata pri sniženom pritisku, potpuno razdvajanje geranil-acetata nije bilo moguće postići. Međutim, prisustvo geranil-acetata nije umanjilo vrednost frakcionisanog ulja, zahvaljujući njegovom prijatnom mirisu. Radi optimizacije procesa destilacije, sistematski su ispitana tri ključna parametra: tip punjenja kolone, visina kolone i radni pritisak. Dobijene frakcije ocenjene su na osnovu prinosa, čistoće, stepena iskorišćenja i GC-MS analize. U optimalnim uslovima, sadržaj geraniola dostigao je 71,35%, uz stepen iskorišćenja od 71,50%, dok je zbirni sadržaj geraniola i geranil-acetata iznosio 93,67%. Ovo istraživanje pružilo je značajan uvid u optimizaciju vakuumske frakcione destilacije za izolovanje frakcija bogatih geraniolom iz etarskog ulja palmaroze, uz poboljšanje kvaliteta proizvoda i smanjenje termičke degradacije. Dobijeni rezultati doprinose unapređenju tehnologija ekstrakcije bioaktivnih jedinjenja, sa potencijalnom primenom u farmaceutskoj, kozmetičkoj i aromaterapijskoj industriji.

Ključne reči: geraniol, vakuumska frakciona destilacija, etarsko ulje palmaroze, Cymbopogon martinii.