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Isolation of citronellal and geraniol from citronella (*Cymbopogon winterianus*) oil by vacuum fractional distillation: Effect of operating conditions on the separation

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This study used fractional distillation to separate citronellal and geraniol from citronella (*Cymbopogon winterianus*) essential oil to improve their market value. The one-factor-at-a-time methodology investigated operating parameters' optimum conditions and effects, including system pressure, packing types, and column height. All investigations were evaluated based on their main fraction's citronellal and geraniol content and recovery. Regarding the effect of the variables, a higher system pressure improved the separation while increasing the temperature range of each fraction and distillation time. The packing types would also improve the separation by providing a large surface area. Finally, the column height also positively impacted the separation. In the optimum citronella oil fractionation, citronellal content experienced a 2.5-fold increase, from 37.68% to 94.33%. Geraniol purity reached 40.61% from an initial content of 17.33% in the raw CW oil. The distillation could recover up to 90.00% of citronellal and 68.18% of geraniol.

Keywords: citronellal, geraniol, vacuum, fractional distillation, citronella oil.

INTRODUCTION

In recent years, the global demand for natural plant-based compounds in the fragrance, flavor, and cosmetic industry witnessed continuous growth due to the increasing concern for synthetic ingredient's safety[1]. The market size of global essential oil reached over 7.51 billion USD in 2018 and was projected to grow around 9% annually in the 2019–2026 period[2]. Among numerous in-demand phytochemicals, citronellal and geraniol are two of the most preferable. They find extensive use in perfumery[3], pharmaceutical[4], and fine chemical fields[5]. Combined with the natural-originated trend, the isolation of both terpenoids from their parental essential oil is becoming more attractive and possesses a high-profit margin. Citronella (*Cymbopogon winterianus*) is the foremost source of raw materials for producing citronellal and geraniol[6, 7]. Generally, a standard citronella oil on the market would consist of around 31.0–40.0% citronellal and 20.0–25.0% geraniol[8].

During the high-demand period of citronellal and geraniol, Vietnam could significantly benefit by isolating and distributing those compounds owing to the available cultivating area of *Cymbopogon winterianus* (CW). In 2007, Vietnam exceeded Indonesia in terms of citronella oil production yield (more than 200 tonnes per year)[9]. However, Vietnam has exploited this advantage ineffectively. In 2005, the annual export of essential oils and fragrances generated only 750 thousand USD while importing up to 1880 thousand USD[10]. The main reason for this is the quality of the exported raw oils. Low-quality oils would lessen their global market value[11]. Therefore, a purification (or refining) of untreated oils is a must to improve their market value and ensure significant constituent quality. In raw essential oil, some constituents, even with a minor content, could distort the main component's original odor and degrade the quality of final products[1, 12]. Thus, the essential oils less attract customers and also present a low market value. Besides, the composition pattern of essential oil quickly varies with each production batch due to differences in genetics, growing conditions, and weather. Hence, the quality and properties of the essential oil would be hard to control. As a result, essential oils are limited in fine chemistry and pharmaceutical production despite their significant bioactivities[13].

Supercritical fluid extraction and fractionation (SFEF), fractional distillation, and chromatography techniques were commonly considered to refine the essential oil. The SFEF method varies the process temperature and pressure to maximize the solubility of target compounds in the supercritical fluids[14]. Most SFEF studies currently focus on combining with raw material extraction to remove nonvolatile molecules such as waxes[15, 16] or eliminating hydrocarbon terpenes from the raw essential oils[17, 18]. There is a lack of SFEF research to purify only one or two target compounds in raw oils since it is rare that there is a condition for supercritical fluids to dissolve only the favored compounds[14]. To find such conditions requires numerous studies on optimization, tremendous energy, and capital consumption. For the chromatography methods, the large-scale process consumes a large amount of organic solvents and gives rise to cost and pollution concerns. On the other hand, fractional distillation becomes a cost-effective, simple technique to separate the volatile oils into various fractions according to their boiling points[12]. With a considerable difference in the constituents' volatility, this method could completely separate the main components[19].

In several studies, the impressive separation efficiency has been discussed regarding the fractional distillation of citronella oil. Beneti *et al.* purified citronellal and geraniol content up to around 92% and 48% from the initial content of 40% and 18% in the raw CW essential oil. The distillation was conducted on a Raschig-packaging

borosilicate column, with an inner diameter of 15 mm and length of 1.5 m at the reflux ratio of 10:1 and ten mbar absolute pressure[20]. Another study by Anwar *et al.* focused on the distillation of a plate column instead of a packed one. The isolation occurred at a near-absolute vacuum with a reflux ratio of 5:10, allowing citronellal to be purified up to 90.10% from an initial content of 35.72%[21]. Besides validating the performance of the distillation methods, more research has paid attention to how the operating conditions affected the degree of citronella oil separation. Agustian *et al.* investigated the effect of operating pressure and reflux ratio on citronellal purity when fractionating citronella oil. Three pressure values (40, 60, and 80 mmHg) and reflux ratios (10:10, 20:10, and 30:10) were chosen for experiments. The final result indicated that the citronellal content peaked at 60 mmHg with a reflux ratio of 20:10. Owing to the experiments, the fractionation achieved the highest citronellal content of 96.10%[22]. Another vital process variable, column height, was considered by Warsito *et al*. They conducted the distillation of citronella oil on packed columns with two height levels, namely 1 and 2 meters. The process operated at 10 mmHg with an unspecified reflux ratio. The result indicated the higher column height would enhance the levels of separation. At the height of 1 meter, citronellal reached only 23.26% whereas the content achieved 88.43% with the 2-m column[23].

From the above review, the fractionation procedure is often operated *in vacuo* to prevent the constituents to thermally decomposing and shorten the distillation time[12, 24]. Under vacuum conditions, most studies proposed a significant increase in citronellal content after isolation on a fractionating column[20–23]. However, some papers only evaluated the performance of the fractionation on the purity and ignored the yield[20, 25]. Meanwhile, the others either mentioned or graphed the yield data but did not discuss and assess solely the effect on purity[21–23]. Moreover, some investigations were conducted only on a small number of milestones and provided only a small picture of the impact of the variables, such as Warsito *et al*.[23]. Hence, there is a need to expand experiments to more values to see the whole pattern effect on citronellal purity and yield.

This study will conduct the fractional distillation of citronella at different system pressure, packings, and column heights. The variables' effect on the process and the distillation conditions achieving the highest citronellal and geraniol purity and recovery would be considered from those experiments. With a simple technique based on considerable differences in the volatile ingredients, this method could completely separate the main components[19].

MATERIAL AND METHODS

Source of Essential Oil

The essential oils used in this study were extracted from the leaves of *Cympobogon winterianus* by a steam distillation system for 4 hours. The oil yield from the distillation process reached 13.5 kg of essential oils per 1 ton of fresh leaves. The raw materials were harvested in Daklak Province, Vietnam, in March 2021 before feeding to the oil extraction. The obtained oils were then stored in sealed HDPE containers at room temperature to avoid direct sunlight conditions.

Description of Vacuum Fractional Distillation System

The distillation system is described in Figure 1. To initiate the experiment, the essential oil was fed to the bottom flask (3). An electrical mantle (1) was set up to supply the heat to the system via a heat-transfer oil bath (2). During the distillation, the vapor passed through the still head and condensed at a Liebig condenser (6). The cooling water for the condenser was maintained at 5 ^{o}C and circulated by the chiller (7) (Lauda Ecoline R215 Staredition, LAUDA DR. R. WOBSER GMBH & Co. KG, Germany). The vacuum inside the system was produced and kept constant by the vacuum pump (12) (Edward RV5F, BOC Edwards, UK). Cold traps (10) and a 10L pressurized tank (11) were installed to protect the pump from external vapors. Meanwhile, a pressure controller (13) is coupled with the pump system to display and control the pressure. The temperature at the feed flask and three-way adapter were monitored using temperature sensors (T1, T2) (Thermocouple Type K M6 2 m, China) after the first drop of distillate. The MAX 6675 modules (Maxim Integrated, United States) were connected with a microcontroller (T4) (Arduino Uno Atmega328P, Adafruit Industries, United States) to decode the signal sent by the sensors and display them on a monitor screen (T3) (Fig. 1).

Operating Procedure of the Fractional Distillation

The raw essential oil would be first decanted with 1.0 gram of sodium sulfate before charging to the feed flask. The heat load and temperature of cooling water were kept constant during the process. Meanwhile, the system pressure was either held steady or followed by a specific program. After the first drop of the distillation, the temperature at the distilling head and pot was tracked at a one-second interval. When splitting the products into different fractions, the multi-limb product receiver was rotated to diversify the distillation to other containers. When the still head temperature started to drop by 10 ^{o}C, the experiment was shut down. The products were then collected, stored at room conditions, and analyzed quantitatively and qualitatively.

Investigation of the CW Oil Fractional Distillation Pattern

An experiment was performed on a 300-mm Hempel column filled with small Fenske helices (Fig. 2) at the absolute pressure of 60 mmHg to explore the fractional distillation pattern of CW oil. The operating procedure was the same as described in the prior section. After the process, the feed and all fractions were then analyzed on a GC-MS system to study their content.

Investigation of the effect of variables on distillation process

Three operating variables were investigated, namely system pressure, packing types, and column height. The experiments followed the one-factor-at-a-time methodology. The effect of each factor was studied by experiment at multiple levels while the others remained

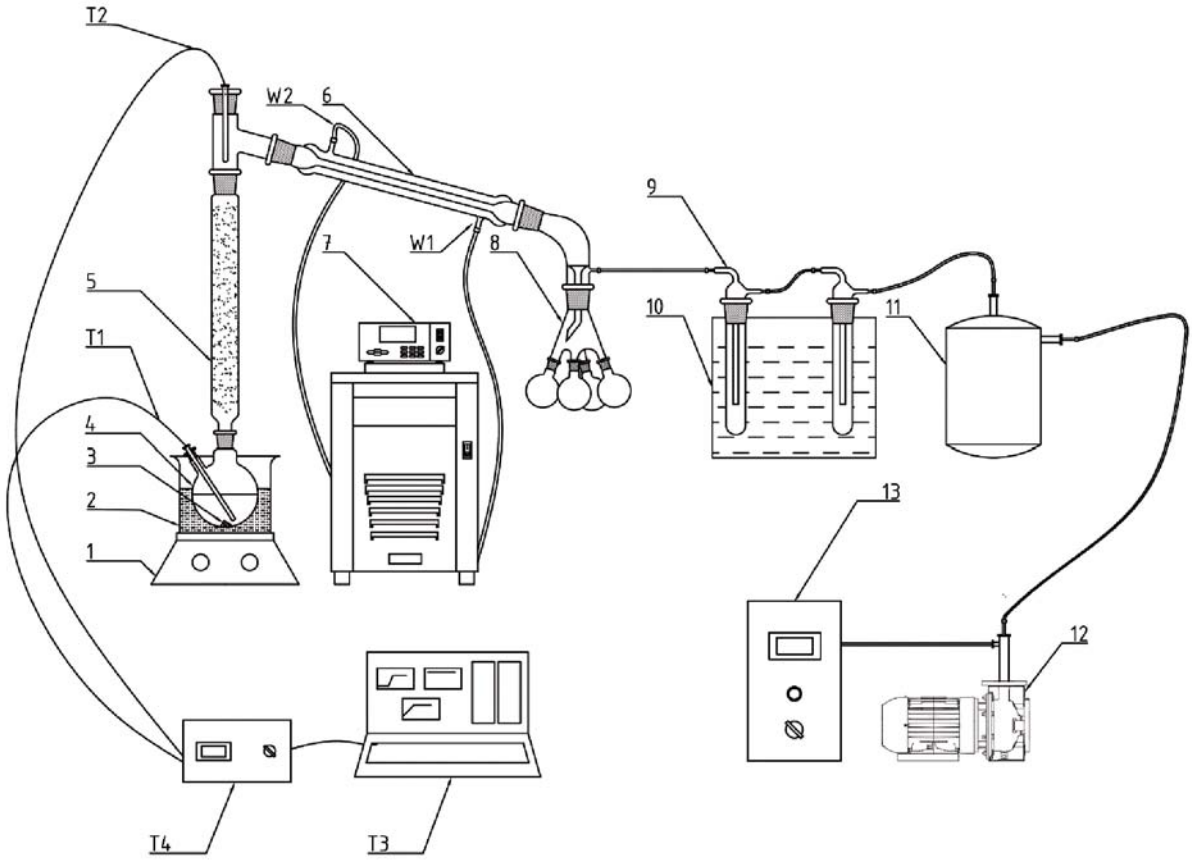


Figure 1. Schematic diagram of the fractional distillation system. [1]Reboiler, [2]Oil bath, [3]Boiling stones, [4]Feed flask, [5]Distillation column, [6]Liebig condenser, [7]Chiller, [8]Multi-limb product receiver, [9]Cold trap, [10]Cold water bath, [11]Pressurized tank, [12]Vacuum pump, [T1, T2]Thermocouple probe, [T3]Temperature monitor screen, [T4]Microcontroller, [W1]Cooling water inlet, [W2]Cooling water outlet

constant. The list of variables and their milestones are summarized in Table 1.

Table 1. Various operating parameters of the fractional process

Research order	1	2	3
Factors	[a]SP (mmHg)	[b]PT	[c]H (mm)
Milestones	20	Small Fenske helices	200
	40	Large Fenske helices	300
	60	Wire mesh	400
	80	Fenske spiral prismatic	500

[a]System pressure, [b]Packing type, [c]Column height

For packing, four types were purchased from Pingxiang Nanxiang Chemical Packing Co., Ltd., China. The appearance and structure of Fenske spiral prismatic, Fenske helices and wire mesh packings are shown in Figure 1. Table 2 summarizes the abbreviation and properties of those packings used in this study.

In each experiment, the mass of all fractions (including the bottom one) was measured to study the yield distribution. Meanwhile, only citronellal and geraniol-rich fractions were analyzed on a GC-MS system. The conditions providing the best citronellal purity and recovery would be selected for the later experiments. Equation 1 and Equation 2 illustrated the calculation of those values.

$$\text{Yield} = \frac{\text{Fraction Weight (g)}}{\text{Feed Weight (g)}} \times 100\%$$

Equation 1. Fraction yield calculation

$$\text{Recovery} = \text{Yield} \times \frac{\text{Constituent content in fraction}}{\text{Constituent content in feed}} \times 100\%$$

Equation 2. Constituent recovery calculation

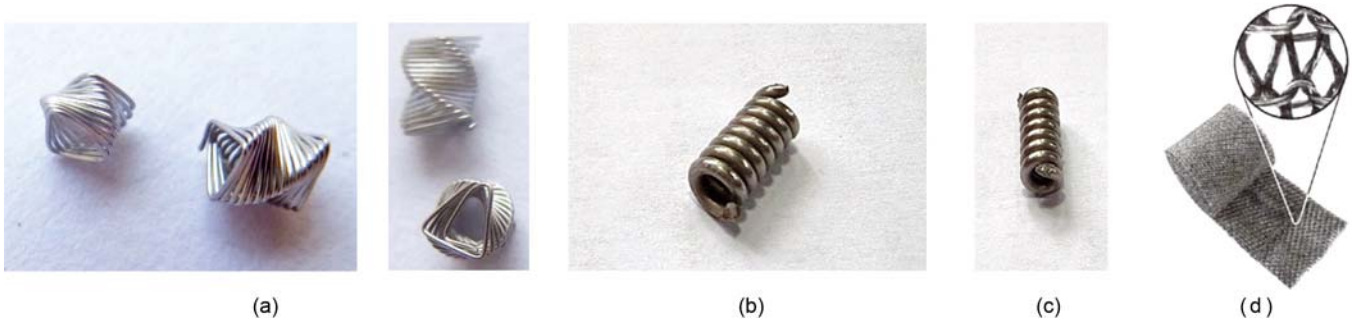


Figure 2. Packing types were used in this study. Reproduced from[26]. (a) Fenske spiral prismatic, (b) Large Fenske helices, (c) Small Fenske helices, (d) Wire mesh

Table 2. Abbreviation and properties of four packing types

Abbreviation	Packing Types	Dimension	[a]Packing Density (m^3/m^3)
M	Wire mesh	Standard Mesh	0.72
SS	Small Fenske helices	D × H = 2 mm× 10 mm	0.85
LS	Large Fenske helices	D × H = 4 mm× 10 mm	0.70
F	Fenske sprial prismatic	D × H = 1 mm× 1 mm	0.96

[a]Data were supplied by the vendors (Pingxiang Nanxiang Chemical Packing Co., Ltd., China)

GC-MS Chromatographic Analysis

The chromatography was performed on an HP-5MS column (30 m 0.25 mm 0.25 μm) using helium as a carrier gas with a flow rate of 1 mL/min. The chromatography section (Agilent G1530A, Agilent Technologies, United States) was coupled with an Agilent mass spectrum detector (Agilent 5973N, Agilent Technologies, United States). The ionization energy was 70 eV, the ionization source temperature of 220 °C, and the mass scan range was from 40 to 400 amu. The sample was diluted in acetone to a concentration of 1000 ppm. The injection volume was 1,0 μL at 250 °C, with a split ratio of 1:50. The scan regime in the GC-MS was 1 second per turn.

For the temperature program, the column temperature was first set up at 60 °C and maintained for 2 minutes before increasing to 147 °C at a rate of 30 °C/min. At this point, the temperature was kept constant for 2 minutes, slowly increase to 149 °C at a rate of 0.25 °C/min and continued to be at 149 °C for 2 minutes. Finally, the temperature grew to 250 °C with a speed of 20 °C/min and was kept at that value for 10 minutes to elute all constituents out of the column.

RESULTS AND DISCUSSION

Raw Oil Chemical Composition

The GC-MS analysis was first carried out on the feed to identify its chemical composition. Eighteen constituents could be determined from the raw oil, as summarized in Table 3. They were divided into four main groups based on their chemical characteristics. Those with the least retention time, two volatile terpenes, were eluted first with low content, composing limonene (4.21%) and linalool (0.83%). A set of three key components was then observed, namely citronellal (37.68%), citronellol (10.01%), and geraniol (17.33%). A small extent of esters followed the elution of the major constituents, namely citronellyl acetate (3.71%) and geranyl acetate (4.14%). Finally, the rest of the compounds were sesquiterpenes and sesquiterpene alcohols such as β-elemene (3.18%), germacrene D (3.40%), α-muurolene (1.40%), δ-cadinene (3.81%) and α-elemol (3.38%).

The CW oil in this work shared a similar composition pattern with a typical Java-type citronella oil[29]. Most key constituents were presented within the ISO-standard (ISO 3846:2016) range, namely citronellal (31.0–40.0%) and citronellol (8.5–14.0%)[8]. However, the geraniol content (17.33%) was lower than the minimum requirement (20.0%)[8]. As shown in Table 4, other studies revealed many components found with several deviations in their content. For example, citronellal was slightly higher concentration than in this study (37.68%), comparing to the result reported in Thailand (30.59%)[30], India (32.70%)[31], and Brazil (36.10%)[32]. Meanwhile, the opposite trend was observed with the geraniol content (17.33%). This content was lower than the analysis from the previous researches, namely 18.17%, 19.90%, and 26.70% proposed by Songkro *et al.*[30], Lorenzo *et al.*[32], Kakaraparthi *et al.* [31], respectively. Three lowly volatile sesquiterpenes were reported as trace (less than 1.0%) in the others but occurring with considerable content in the raw oil, such as germacrene D (3.40%), α-muurolene (1.40%) and δ-cadinene (3.81%). In summary, this variation performed high citronellal and low geraniol content while composing a fair amount of high-boiling impurities. These deviations above can be explained by

Table 3. Raw CW oil composition used in this work

Compound	[a]RT (min)	[b]%	[c]BP [°C]	[d]Ref
limonene	8.47	4.21	178	[27]
linalool	9.55	0.83	198	[27]
citronellal	10.40	37.68	205	[27]
isopulegol	10.59	0.51	214	[28]
citronellol	11.50	10.01	225	[27]
neral	11.77	0.34	228	[28]
geraniol	11.91	17.33	229	[27]
geranial	12.17	0.64	229	[27]
citronellyl acetate	13.26	3.71	242	[28]
geranyl acetate	13.67	4.14	244	[28]
β-elemene	14.00	3.18	252	[28]
germacrene D	15.24	3.40	264	[28]
α-muurolene	15.41	1.40	[e]NA	NA
δ-cadinene	15.69	3.81	NA	NA
α-elemol	16.00	3.38	NA	NA
(-)-globulol	16.41	0.57	NA	NA
τ-cadinol	17.14	0.85	NA	NA
Total		96.00		

[a]Retention time (min); [b]Percentage area in GC-MS chromatogram; [c]Boiling point at ambie nt pressure, 760 mmHg; [d]Reference of the boiling point; [e]Not available

Table 4. Raw CW oil composition this study and from different regions (%)

Compound	This study	[a]ISO range	[b]Thailand	[c]India	[d]Brazil
limonene	4.21	2.0–5.0	4.59	3.10	3.00
linalool	0.83	0.5–1.5	1.20	0.80	0.60
citronellal	37.68	31.0–40.0	30.59	32.70	36.10
isopulegol	0.51	0.5–1.7	1.90	0.40	0.10
citronellol	10.01	8.5–14.0	19.30	6.90	9.90
neral	0.34	[e]~	[f]–	0.70	0.40
geraniol	17.33	20.0–25.0	18.17	26.70	19.90
geranial	0.64	0.3–1.0	–	1.00	0.60
citronellyl acetate	3.71	2.0–4.0	4.43	3.80	3.50
geranyl acetate	4.14	2.5–5.5	–	9.00	3.80
β-elemene	3.18	0.7–2.5	3.65	0.70	1.60
germacrene D	3.40	1.5–3.0	–	0.40	2.60
α-muurolene	1.40	[e]~	–	0.20	0.40
δ-cadinene	3.81	1.5–2.5	–	0.80	1.90
α-elemol	3.38	1.3–4.8	3.34	7.20	5.80

[a]ISO Standard (ISO 3846:2016) on the quality of Java-type citronella oil [8], [b]Songkro *et al.* (2012) [30], [c]Kakaraparthi *et al.* (2014) [31], [d]Lorenzo *et al.* (1999) [32], [e]Not mentioned, [f]Not detected

difference in genetic diversity, habitation, harvest time, climate, and soil conditions[29, 31, 33].

Fractional Distillation of *Cymbopogon winterianus* Oils

The fractional distillation pattern provided information on the number of possible fractions, their temperature range, yield, and composition when performed on a specific feed. Specifically, there were four significant intervals based on the boiling point of CW oil its constituents (Table 3). In general, those constituents gathering in the same distillate would have close volatility. Hence, the number of fractions would correspond to how many constituents have enough difference in their volatility. Limonene and linalool, the most volatile ingredients which distilled in the first interval, followed by citronellal in the succeeding stage. At the end of the distillation, the third fraction showed the transfer from citronellal to geraniol and citronellol while the fourth contained most of these two compounds. The close boiling point between citronellol (225 °C) of citronellol and geraniol (229 °C) adversely affected the separation efficiency. This phenomenon was observed for several adjacent compounds in this range, such as neral (229 °C), geranial (229 °C), citronellyl acetate (242 °C), and geranyl acetate (244 °C). As a result, there is a significant chance for them to present concurrently in the third interval. Eventually, the remaining at the distilling pot would be the fourth fraction. This products could contain citronellol, geraniol, and all lower volatile constituents that had not been removed yet.

To valid the above prediction and determine the specific temperature range of each interval, an experiment was performed on a 300-mm Hempel column filled with small metal helices at the absolute pressure of 60 mmHg. The temperature records at the distilling head and pot during the fractionation were shown in Figure 3a.

As shown in Figure 3a, the column head configuration was steady at F2 fraction (126–127 °C) and F4 fraction (146–148 °C. Those leveling out could be indexed to the distillation of either a single component or a mixture with a constant composition since their vapor temperature was maintained during the boiling period. This could be concluded that the fraction at around 126 °C was substantial in citronellal and the other was mainly composed of citronellol and geraniol. The transition between those plateaus at 128–145 °C (F3 fraction) presented for the transition between two main fractions (F2 and F4). On the other hand, the first transition periods (76–125 °C) might correspond to the distillation of lighter terpenes such as limonene and linalool. Though limonene and linalool mainly were purified in this stage, the temperature increased significantly instead of slightly fluctuating as described above. The possible explanation was inconsiderable limonene and 1,8-cineole

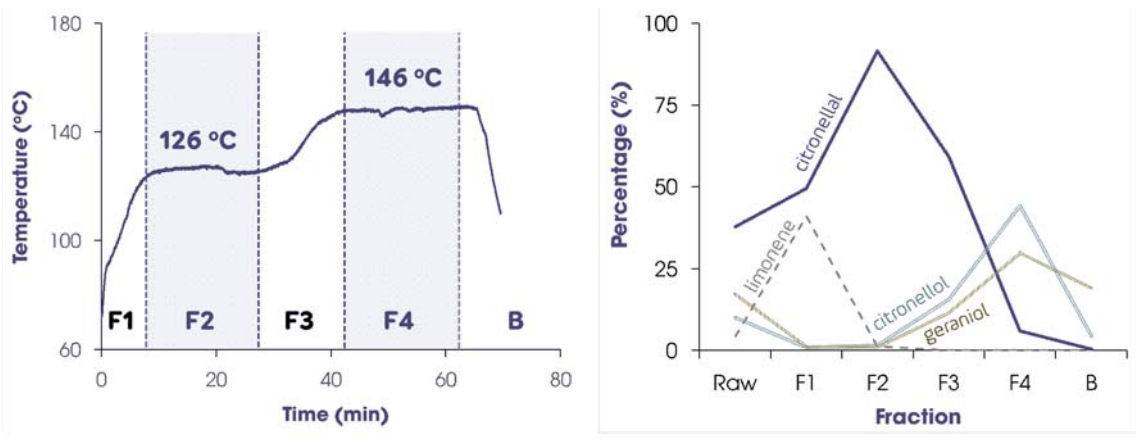


Figure 3. The profile of the CW oil fractions. (a) Temperature profile at the top of the column, (b) Composition profile

in the original oil (only 5.04% in total). In this experiment, the power input from the heating mantle could gasify a vast amount of constituents because of the reduced vaporization enthalpy at low system pressure[34]. This energy supplied was too much to evaporate only a tiny amount of limonene and 1,8-cineole. Hence, the adjacent constituents such as citronellal which distilled by the excess power input. This phenomenon led to the simultaneous vaporization between limonene, linalool, and citronellal; changed the vapor composition as well as the temperature, continuously.

The chromatography analysis was used to identify the major constituents in each fraction. The result of Figure 3b described the change in the composition of all four intervals during the fractional distillation. As shown in Figure 3b, limonene was the first expected compound to be distilled, which obtained a high purity of 40.97% at the F1 fraction. The stripping of limonene from the batch feed rapidly occurred since the content was negligible immediately after the first interval (1.20% at F2 fractions and not detected at F3, F4, and B fraction). The citronellal content achieved the highest value (91.58%) at F2 fraction but was still considerable at the F3 (59.10%) and F4 (6.02%) fraction before mainly being removed from the residue (0.36%). The contamination on the other fractions could reduce the recovery of citronellal from the raw essential oil and the profit from selling high-purity citronellal.

The separation of citronellol and geraniol was not efficicent because of the presence of rhodinol. Rhodinol was a mixture of citronellol and geraniol which primarily distributed in the last two distillate fractions, F3 (15.72% citronellol, 11.56% geraniol) and F4 (44.21% citronellol, 29.88% geraniol). In addition, the residue at bottom flask after the distillation also included an amount of citronellol (4.53%) and geraniol (19.16%). This indicated their incomplete removal from the feed.

The yield of each fraction was a mandatory criterion since this factor dramatically impacted the production profit. If the fraction allowed a high purity of key constituents, but with only a tiny amount, the process was inefficient to produce on a large scale to supply the market. Figure 4 illustrates the yield of each CW oil fraction at 60 mmHg. In the ideal scenario, F2 fraction consisted mainly of pure citronellal, which would yield 37.68% (citronellal composition in the raw material). Meanwhile, F4 fraction included citronellol and geraniol, which was about 27.34% (total rhodinol composition).

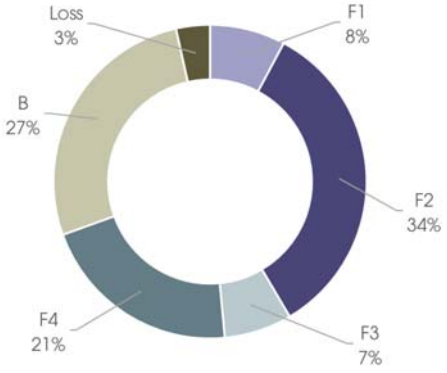


Figure 4. The yield of each fraction of the CW oil experiment at 60 mmHg

Comparing those ideal estimations with the experimental data from Figure 4, the F2 and F4 fraction amount was not significantly different (33.7% and 21.0%, respectively). Hence, the fractionation process could achieve a considerable amount of high-content key constituents with a considerable yield. The loss amount was also acceptable, reaching around 3.5%. In the other studies, the overall percentage loss might range from 1 to 5%[24, 25, 35].

As the present outcome depicted, the CW oil fractionation could achieve highly pure citronellal (>90%) in F2 fraction with an acceptable yield. However, the volatile point was not significantly different which prevented an efficient separation between citronellol and geraniol. The fractional distillation, though, could be used as an enrichment stage. Specifically, citronellol and geraniol were abundant in F4 fraction which required to pass further separation to obtain them separately.

Effect of Operating Pressure on the Distillation

The distillation of parental CW oil was performed on the 300-mm Hempel column filled with small Fenske helices (10 mm x 2 mm i.d.) at four system pressure (20, 40, 60, and 80 mmHg). The fraction composition, yield, citronellal and geraniol recovery were monitored and shown in the following figures for evaluation.

Figure 5 illustrated the top-column temperature profile regarding four system pressures. In general, the distillation process provided only two fractions at 80 mmHg and less than other pressure values. The analysis of two fractions proposed that citronellol and geraniol were not found by distillation at 80 mmHg. The higher the system pressure, the more significant energy to gasify a liquid phase[34]. However, when the pressure continued to increase, the heat supplied to distillate vapor out of the column might exceed the current input power of the heating mantle. As a result, the low-volatile constituents such as citronellol and geraniol could not present in the products.

The result of Figure 5 showed that the decrease in system pressure reduced the distillation time and temperature range of all fractions. The distillation time was gradually declined (from around 70 to 50 minutes) in the direction of pressure decrease (from 80 to 20 mmHg) At the lowest pressure (20 mmHg), the temperature for distillation at fractions F2 and F4 was lower (starting from 100 °C and 117 °C, respectively), instead of 126 °C and 138 °C at 80 mmHg (Fig. 6). The data of temperature range corresponding to each fraction were summarized in Table 5. The lesser of both fraction temperature and distillation time would benefit the pure flavor production from essential oil. Lower temperatures prevented the possibility of thermal degradation into disagreeable by-odor, breaking the essence of main constituents[12]. The less distillation time would also consume a lower amount of energy to supply to the system.

Table 5. The temperature range of each fraction at various pressure in CW fractionation

Fraction	Temperature Range (°C)			
	20 mmHg	40 mmHg	60 mmHg	80 mmHg
F1	70–99	78–114	83–125	88–133
F2	100–109	115–120	126–127	134–136
F3	110–116	121–130	128–142	–
F4	117–123	130–136	142–148	–

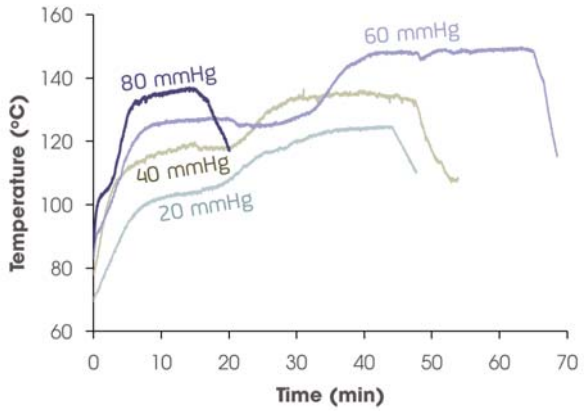


Figure 5. The top temperature profile at various system pressure

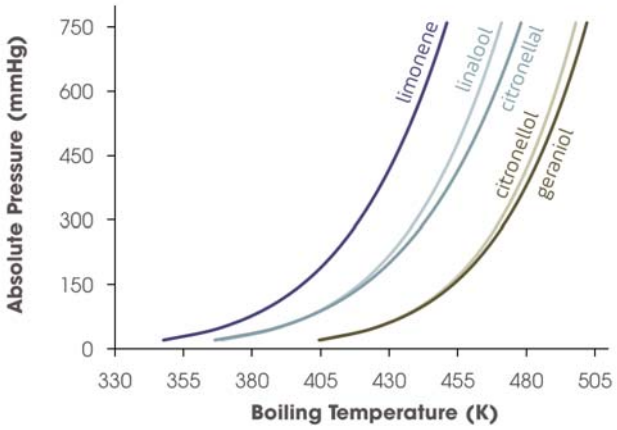


Figure 6. The pressure–boiling temperature profile of CW oil major constituents. Adapted from[36]

As shown in Figure 7a, the separation efficiency in F2 fraction was greatly affected by the system pressure, as the higher system pressure led to higher citronellal and lower impurities (limonene, linalool, citronellol, and geraniol) content. When the pressure was increased from 20 to 60 mmHg, the purity of citronellal was improved by almost 1.5-fold (from 65.20% to 91.58%). However, the rate of increase in purity became slower for higher-pressure levels. At 60 mmHg and 80 mmHg, the F2 fraction consisted of almost the same amount of citronellal, namely 91.58% and 91.04%. The same phenomenon could be observed at other constituents. There was a sharp decrease in limonene content, from 9.83% (20 mmHg) to 2.46% (60 mmHg), before reaching a plateau around 1.2% at 60–80 mmHg. The steep decline could also be seen with citronellol and geraniol. The percentage of citronellol in the F2 fraction changed from nearly 6% (20–40 mmHg) to 1.7% at the other pressures. Meanwhile, those values relating to geraniol were 7% and 1%, respectively.

The above relationship could be attributed to two different sources: liquid-vapor contact and relative volatility. Regarding the former, lowering the pressure level allowed a higher expansion of vapors and gases, resulting in a massive decline in vapor density[37]. Hence, there are fewer vapor molecules per unit volume inside the column, which reduced the contact rate between liquid and vapor phases and limited the separation efficiency[37, 38]. Relative volatility was also a concern affecting the degree of separation. A reduction in the absolute pressure typically resulted in a lower boiling

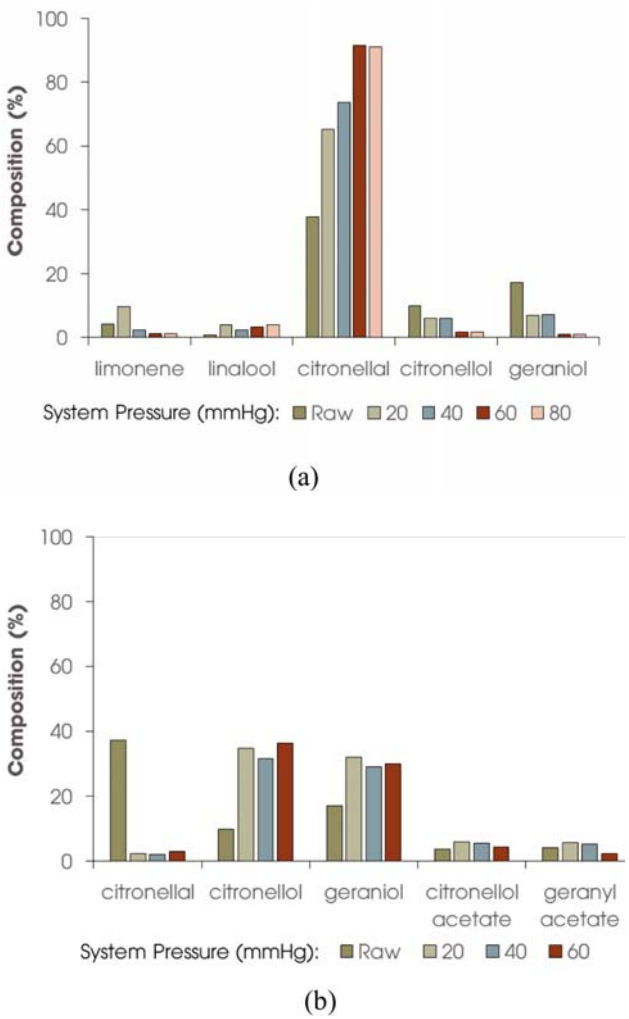


Figure 7. Effect of system pressure on the composition of the distillate (a) F2 fraction, (b) F4 fraction

temperature, however, at a different rate. Therefore, the difference in boiling point between constituents, representing their relative volatility, could rise or fall in a given case depending on the investigated system [38].

For the CW oil, Figure 6 provided that the boiling point variation of citronellal and its adjacent components (limonene, linalool, citronellol, and geraniol) increased significantly as the pressure improved, leading to the higher efficient separation for higher pressure. However, if the system pressure continues to increase, the difference in their volatility would rise to a level sufficient for effective separation, and any change in pressure would result in a minor improvement in the degree of separation, explaining the tendency in Figure 7a.

For the F4 fraction, Figure 7b showed that the pressure influence on distillated composition was negligible. The citronellol and geraniol content did not exhibit a significant change with all pressure levels. The purity of citronellol in F4 fraction changed from 34.70% (20 mmHg) to 31.54% (40 mmHg), then slightly improved to 36.27% (60 mmHg). Meanwhile, geraniol content fluctuated in the range of 29.0–31.9% in the direction of increasing pressure from 20 to 60 mmHg. A similar tendency could be observed at citronellal (2.0–3.0%), citronellol acetate (4.5–6.0%), and geranyl acetate (2.4–5.8%). In this case, the increase in pressure did not perform the same effect as citronellal in F2 fraction. The boiling point difference of those constituents in F4 fraction was almost indifferent

even at atmospheric pressure (Table 3), which prevented a fractionation between them. Several studies also reported the inseparable fraction of rhodinol, even at a much higher column height and reflux ratio than this work[23, 35, 39]. The comparison was summarized in Table 6.

Rihayat *et al.*[39] and Warsito *et al.*[23] showed the most impressive results when the geraniol content was around 58%. Meanwhile, there was still a large amount of citronellol in the fraction at nearly 24% despite various operating parameters. Another study by Achmad *et al.*[35] proposed a much lower level of geraniol content while including a high amount of citronellol, namely 37.27% and 45.42%, respectively. The above evidence showed that the distillation method was an inappropriate way to obtain geraniol separately, even when different pressure and column height levels were used.

The variation of the yield fraction against system pressure (Fig. 8) followed a reverse trend between the main fractions (F2 and F4 fractions) and the transition ones (F1 and F3 fractions). The former amount decreased gradually, whereas that of the latter increased along with the system pressure rise. A 10-percent drop in the yield of the F2 interval was observed when vacuum pressure decreased from 20 mmHg (42.30%) to 80 mmHg (33.70%). This decline in F4 fraction was almost the same (nearly 10%), from 34.20% at 20 mmHg to 24.50% at 60 mmHg.

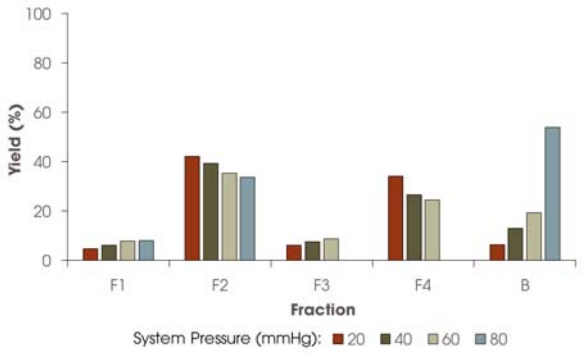


Figure 8. Effect of system pressure on the yield of each fraction

The decrease in the yield of the F2 fraction could have originated from the better separation efficiency at higher pressure levels. Figure 7a describes how the impurities (limonene, geraniol, and citronellol) composition decreased when the pressure varied from 20 mmHg to 100 mmHg. As a result, the F2 fraction now received less amount of those constituents and decreased its yield.

Meanwhile, though the separation efficiency did not improve at higher pressure with F4 fraction, the geraniol-rich distillate still observed its reduction. Therefore, an additional effect of higher pressure must be presented. Increasing the pressure decreased the volatility of constituents and limited their vaporization process[34]. As a result, the same power input at the heating mantle could vaporize only fewer constituents from the feed, reducing the fraction yield. At 80 mmHg, the volatility of geraniol decreased to such a level that the heating input provided was insufficient to vaporize and transport it along the column, resulting in the disappearance of this compound in the product.

The overall citronellal recovery peaked at 85.97% at 60 mmHg (Fig. 9a). The recovery significantly declined for both the lowest and highest-pressure levels, particularly 73.13% and 81.36% at 20 and 80 mmHg, respectively. The pressure level of 60 mmHg allowed both the highest citronellal content (91.58%) and recovery (85.97%) in the F2 fraction. Hence, 60 mmHg was selected as an optimum pressure value for citronellal fractionation for further experiments.

The recovery of geraniol reached the highest value of 62.86% at 20 mmHg and decreased sharply at higher

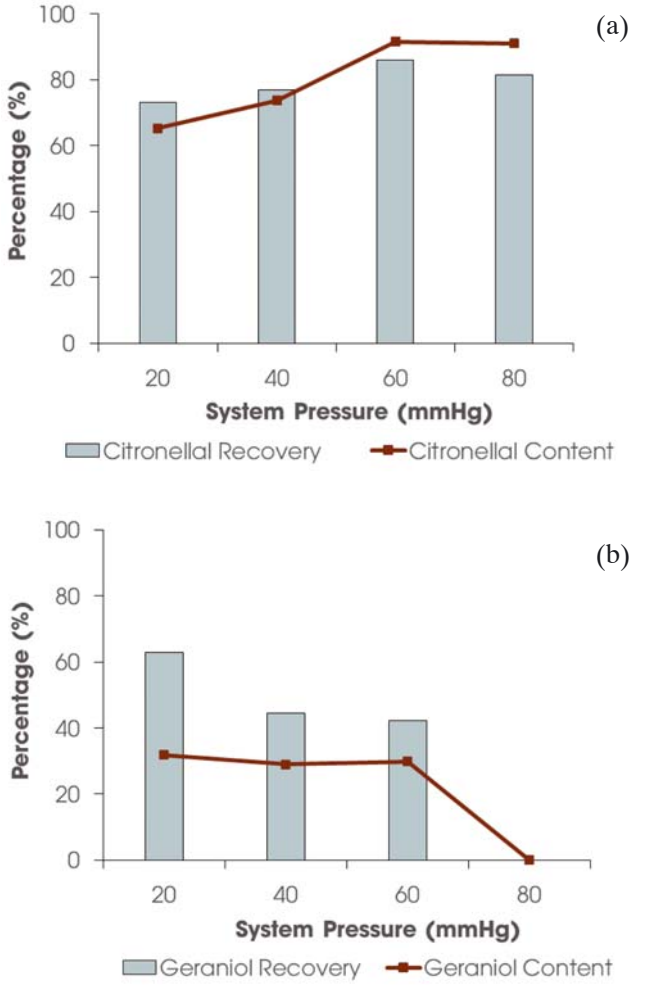


Figure 9. Effect of system pressure on the content and recovery of the key constituent. (a) In F2 fraction, (b) In F4 fraction of the key constituent (a) In F2 fraction, (b) In F4 fraction

Table 6. Literature review of rhodium-rich fraction composition in CW fractionation

Study	[a]H	[b]P	[c]R	Citronellol (%)		Geraniol (%)	
				Raw	Fraction	Raw	Fraction
Current	300	20	0	10.01	34.70	17.33	31.90
[35]	1000	10	3:1	13.80	45.42	12.70	37.27
[23]	2000	30	[d]–	17.62	24.48	10.92	58.26
[39]	[e]ASTM	1	–	9.57	23.50	20.32	57.39

[a]Column height (mm), [b]System pressure (mmHg), [c]Reflux Ratio, [d]Fraction achieving the highest content of rhodinol, [e]Not mentioned in the study, [f]Using the ASTM D1160 Vacuum Distillation Apparatus

pressures (down to 42.18% at 60 mmHg and 0% at 80 mmHg). The different changes in geraniol content and yield explained this tendency (Fig. 9b). When the pressure dropped from 80 mmHg to 20 mmHg, the yield of the F4 fraction increased considerably, whereas its content mainly remained constant due to the inefficient separation. Therefore, 20 mmHg was the suitable value of pressure to purify geraniol from its parental oils.

In conclusion, to utilize the highest recovery of both citronellal and geraniol, a pressure program should be conducted. At the early stage of the distillation, the pressure of 60 mmHg was chosen to allow the most outstanding amount and purity of citronellal in the F2 fraction. By then, the fractionation would be performed at 20 mmHg to obtain geraniol in the F4 fraction. This step pressure program combining the optimal pressure relating to both constituents would be applied in all other processes.

Effect of the different types of packing on the distillation

The packing effect on the fraction yield, content, and recovery of citronellal and geraniol was considered. The fractionation was conducted on a 300-mm Hempel column filled with four different packings on a pressure program (60 mmHg at first and 20 mmHg at last). Large Fenske helices, small Fenske helices, Fenske spiral prismatic, and wire mesh structure packings were applied respectively into the packing bed.

Figure 10 illustrates the different effects of two sets of packing types on the citronellal content of the F2 fraction. Meanwhile, the F2 fraction is composed of nearly 70% citronellal content with wire mesh packing and large Fenske helices, less than 20% compared with other types (91% using small Fenske helices and Fenske spiral prismatic). Citronellol and geraniol content experienced the reversed pattern which was higher with the former group (7–9%) and lower with the latter (1–3%). In addition, the substitute of wire mesh structure packing by the other types reduced limonene content from 4.93% to around 0.6–1.2%, respectively.

In this case, the difference in the contact area among the packings could explain the tendency above. The large dimensions of wire mesh packing and large Fenske helices (Table 2) attributed a reduction in the number of packing units per volume, leading to a decline in their surface area per volume. As a result, the liquid and vapor phases had a smaller contact area to transfer constituents and reduced the separation efficiency.

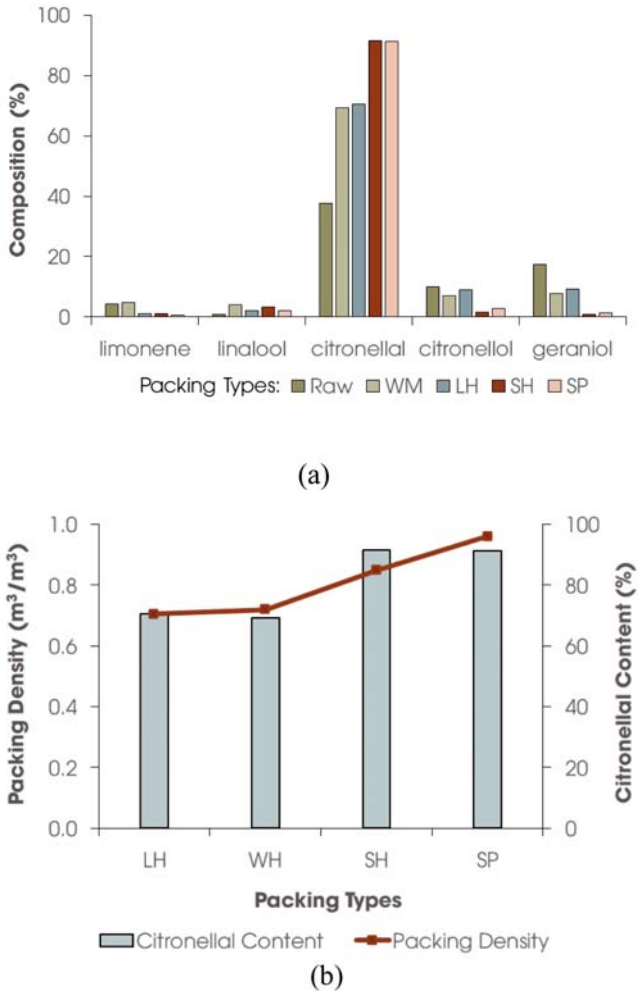


Figure 10. Effect of packing types on the F2 fraction composition. (a) For major consitutents, (b) For citronellal. [WM]Wire mesh structure packing, [LH]Large Fenske helices, [SH]Small Fenske helices, [SP]Fenske spiral prismatic

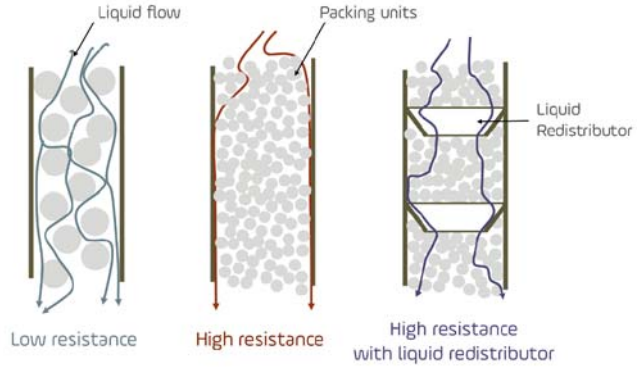


Figure 11. Side-wall effect in the distillation tower

However, the separation efficiency was almost the same between small Fenske helices and Fenske spiral prismatic despite a considerably smaller size of the latter (Figure 10). Therefore, the smaller size of packing units could negatively impact the separation aside from its positive ones. Liquid tended to choose the least resistant path when flowing back to the feed flask[37]. Thenceforth, when the liquid phase passed through high-density packing beds such as Fenske spiral prismatic, it would travel toward the column sidewall to avoid the high motion resistance of the packings (Figure 11). Meanwhile, the vapor phase tended to fill up all the space in the column center. As a result, the contact between the two phases reduced and negatively impacted the degree of separation. On an industrial scale, the large metal-packed tower was often fabricated with the liquid redistributors after each packing bed section to diversify the liquid back to the central column (Figure 11)[26, 40]. However, at the laboratory scale, the fragile material and small size of the glass column made the production of the liquid redistributor complicated.

The unclear pattern of the citronellol, geraniol, and their ester content could be explained by their close boiling points. The improvement in the liquid-vapor area by applying minor packing was not enough to separate them. Nevertheless, if the size of packings reduced to the level of Fenske spiral prismatic, the massive increase in

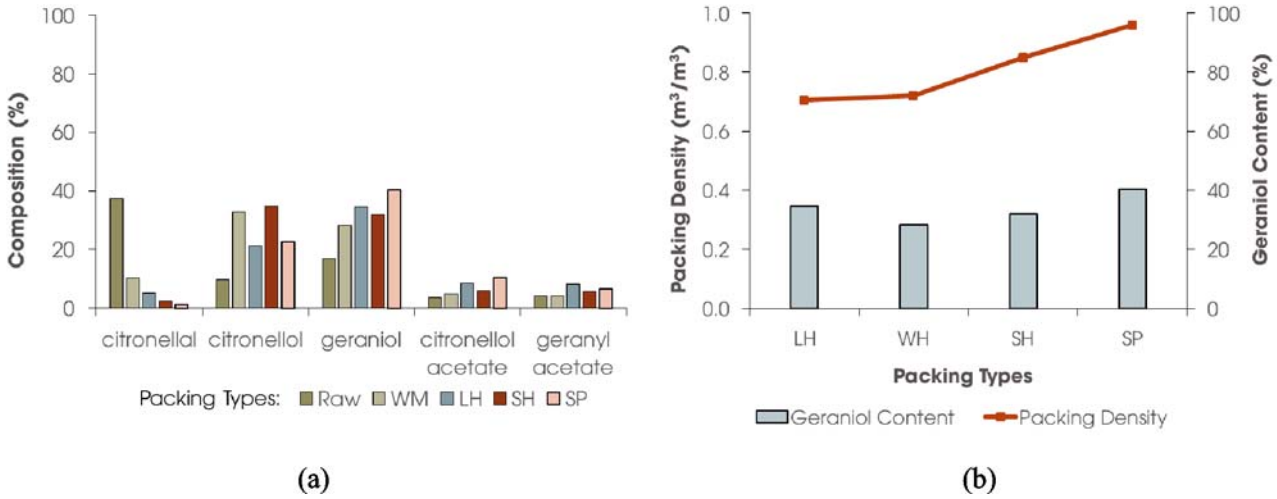


Figure 12. Effect of packing types on the F4 fraction composition. (a) For major constituents, (b) For geraniol. [WM]Wire mesh structure packing, [LH]Large Fenske helices, [SH]Small Fenske helices, [SP]Fenske spiral prismatic

contact area could now slightly improve the purification of geraniol as declared above (40.26% compared to 28–34% with the other packings).

The fraction yield result from Figure 13 revealed that the amount of two main fractions was affected considerably by the packing types. In particular, the wire mesh structure packing allowed the most significant yield of the F2 fraction (42.10%). This yield then decreased gradually with the decrease in packing size, namely 40.10% (large Fenske helices), 35.40% (small Fenske helices), and 33.20% (Fenske spiral prismatic). The yield of the F4 fraction was observed with a similar pattern, reaching highest with wire mesh packing (34.20%) and lowest with packing with the most petite sizing (29.20%).

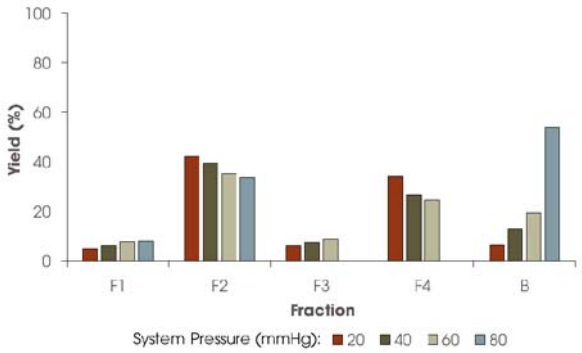


Figure 13. Effect of system pressure on the yield of all fraction. [WM]Wire mesh structure packing, [LH]Large Fenske helices, [SH]Small Fenske helices, [SP]Fenske spiral prismatic

This resulted from the different structures of the packing. The high density of small Fenske helices and Fenske sprial prismatic adhered enough volume of liquid on the surface to those pores, which increased the liquid hold-up and decreased the fraction yield [26]. Besides, the more the amount of packing units per volume becomes, the higher the pressure drop across the beds, which means that the same energy input would be sufficient for less vapor to escape the column. Hence, the decrease in packing size also led to a decline in the vapor load, fraction yield, and an increase in the bottom weight.

In summary, the overall citronellal recovery was maximized with the small Fenske helices (85.97%), as illustrated in Figure 14. Though small Fenske helices did not improve separation efficiency as much as Fenske spiral prismatic, the former allowed a much vaster yield compared to the latter. As a result, for the later set of experiments, small Fenske helices were selected as suitable packing types to obtain the F2 fraction in the fractionation of CW oil. The recovery with other packings was also relatively close to the optimal value, namely 77.21% (wire mesh packings), 74.90% (large Fenske helices), and 80.43% (Fenske spiral prismatic).

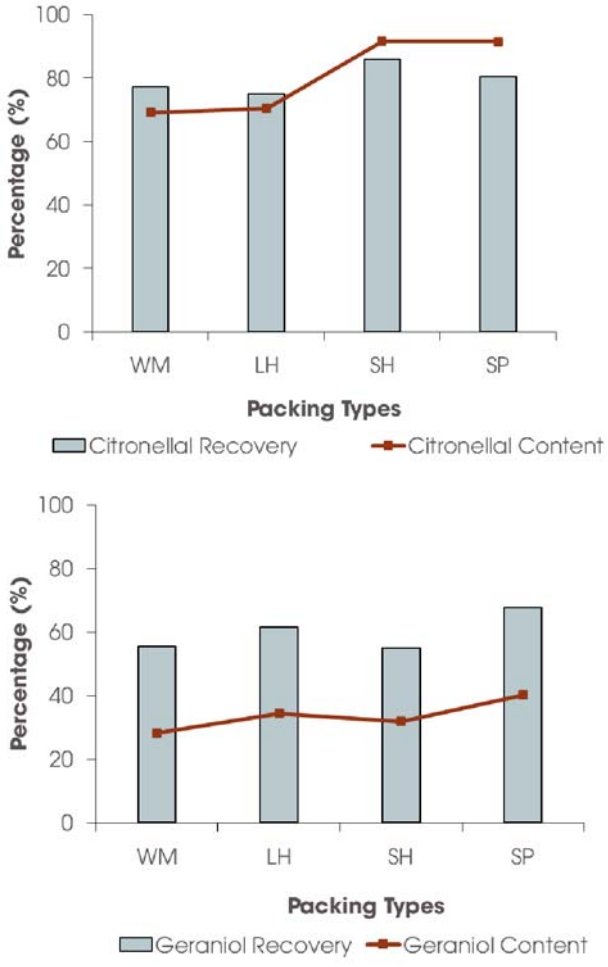


Figure 14. Effect of packing types on the content and recovery of the key constituent (a) In F2 fraction, (b) In F4 fraction. [WM]Wire mesh structure packing, [LH]Large Fenske helices, [SH]Small Fenske helices, [SP]Fenske spiral prismatic

For the F4 fraction, the increase in contact area by decreasing the sizing of packings did not provide a sufficient effect except for the Fenske spiral prismatic. The impressive increase in geraniol content even outweighs the slight decrease in the amount of F4 fraction with this packing type. Hence, the overall geraniol recovery and content reached a maximum value of 67.72% (recovery) and 40.26% (content) with Fenske spiral prismatic.

In conclusion, there are two different optimal packing types for separation: citronellal and geraniol. Hence, in practice, the distillation of citronella oil would need two separate columns. The first one was filled with small Fenske helices to distill the citronellal. The citronella oil was fractionated in this column to obtain the first two fractions (F1 and F2 fractions). When the top temperature started to rise (the distillate was changing to F3 fraction), the operating would be shut down immediately. This process would occur in multiple batches to gather all F2 fractions and the residue at the bottom flask separately. The remaining would then be compiled and fed to the second column filled with Fenske spiral prismatic to collect geraniol. However, to perform a complete separation of one batch, the gathering phase would be passed. The distillation would be conducted first with small Fenske helices for the first two fractions, and the others would be isolated with Fenske spiral prismatic.

Effect of Column Height on the Distillation

This section discussed the relation between the column height and the degree of separation, fraction yield, and overall recovery of citronellal and geraniol in F2 and F4 fractions. Four different levels of height were examined, namely 200, 300, 400, and 500 mm. The distillation was performed on a Hempel column filled with either large Fenske helices (F1 and F2 fraction) or Fenske spiral prismatic (in F3 and F4 fraction). The system pressure was set at 60 mmHg during the collection of the first two fractions and 20 mmHg during all other stages.

Citronellal content in the F2 fraction increased significantly as the column became higher, from 64.81% (200 mm) to 94.33% (400 mm), as shown in Figure 15. However, when the height exceeded 400 mm, a drop in the citronellal purity was observed, which decreased from 94.33% to 88.93% at 400 and 500 mm, respectively. The content variation of other impurities, in reverse, did not experience any significant change against the column height, except at 200 mm with citronellol and geraniol.

The positive correlation between column height and degree of separation was reported in several previous studies[23, 24]. Warsito *et al.* refined citronella oil on a Hempel column filled with Raschig rings on a 2-kg batch[23]. They observed that using a 2-m packaging column instead of a 1-m one leads to an almost 3-fold increase in the amount of citronellal in the top fraction from 31.63% to 88.43%. At higher initial content of constituents, the improvement at higher column height also occurred but with a smaller effect. Do *et al.* provided that the citral content slightly increased from 89% to 93% when the column length changed from 200 mm to 400 mm in the fractionation of *Cymbopogon citratus* essential oil[24].

On a more extended column, besides permitting more vaporization-condensation cycles, the liquid and vapor phases would have more retention time, leading to a higher contact rate between them[24]. Consequently, the increase in column height for the same packing always increases the number of theoretical plates, representing separation efficiency[37].

On the other hand, the negative impact of column height after reaching a critical height was not mentioned in the research relating to the height effect on fractional distillation[23, 24]. In this case, the random packing method could lead to a poor distribution of packing units, especially when using packing with uneven height and diameter as large Fenske helices. Therefore, the rundown of liquid through packing beds may occur in a different channel with the vapor, therefore avoiding the component transfer[37]. The liquid in the column could tend to flow along the column walls for the least resistance (also known as the sidewall effect), while the vapor passes up through the void between packing beds, which also limits their contact. The longer the column is, the worse those phenomena become[37]. When the column reaches a sufficient height, those negative impacts would exceed the enhancement of liquid-vapor contact, and the degree of separation begins to decrease toward higher column height. Though the negative impact could be solved by equipping the system with a liquid distributor, the small diameter and glass material of the column in the laboratory system make the manufacture become intricate.

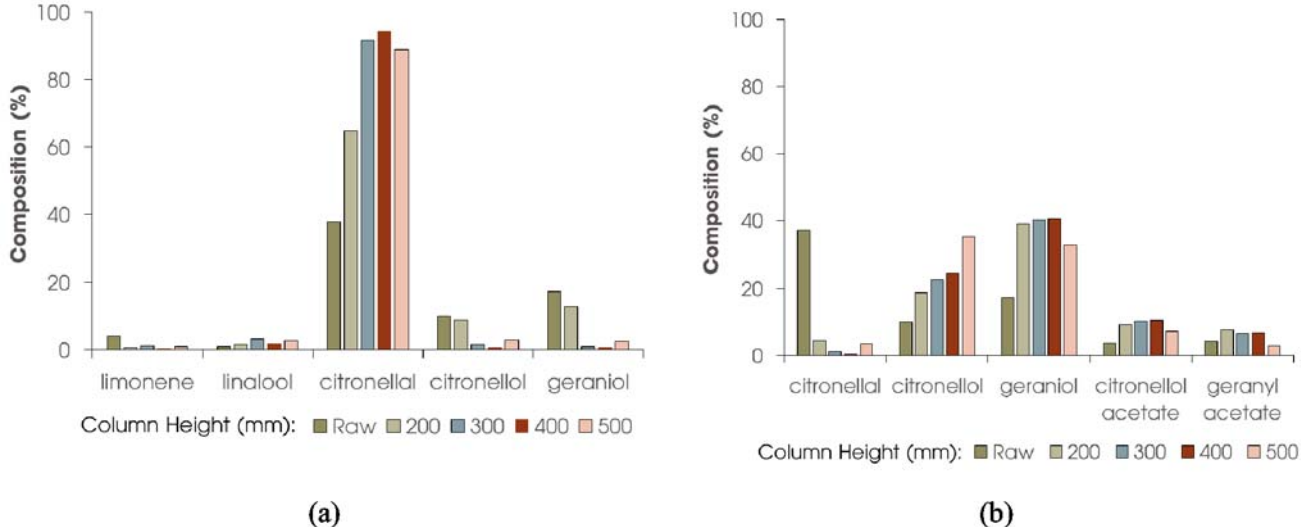


Figure 15. Effect of different column height on the composition of the distillate (a) F2 fraction, (b) F4 fraction

For the F4 fraction, as the height level of the column elevated from 200 mm to 400 mm, the main constituents such as citronellol and geraniol witnessed a gradual increase in their content but at a different rate (Figure 15). Citronellol content improved considerably from 18.66% to 24.56%, while geraniol changed slightly from 39.15% to 40.61%. When the column height exceeded 400 mm, citronellol content continued to increase, achieving 35.20%. In reverse, geraniol decreased its content to 32.80%.

The explanation disclosed in the F2 fraction could apply to this one. There is a positive impact on separation efficiency regarding the column height increase before reaching the critical height. However, the impact was not clear due to the close boiling points between the constituents.

Figure 16 illustrates a significant change between the lowest height and the other levels concerning the yield of each fraction. The decrease rate of F2 fraction amount against column height was high, from 46.60% (200 mm) to 37.1% (300 mm), while much lower toward other values, from 37.1% (300 mm) to 35.0% (500 mm). Meanwhile, the amount of F4 distillate was suddenly lower at 200 mm (18.20%) compared to the height level of 300 mm (29.40%) and 400 mm (24.70%). In this case, the higher column may lead to a better separation. The shortest column (200 mm) performed the worst separation, leading to a high amount of F4 co-distillated with F2 and F3 fractions. As a result, the yield of F2 and F4 fractions was notably different from the other levels.

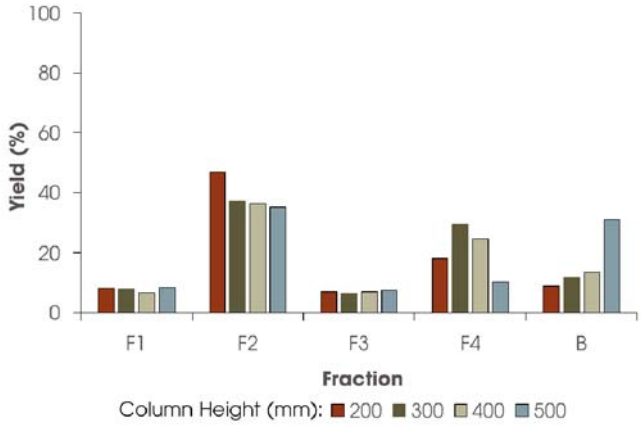


Figure 16. Effect of column height on the yield of all fraction

At 500 mm, another sharp drop in F4 amount was observed, achieving only 10.30% of the total distillate. There was also a considerable change in the range of 400 and 500 mm relating to the yield of residue (13.60% at 400 mm and 31.10% at 500 mm). This change is the result of the high-pressure drop to pass through beds. This decreased the vapor load escaping the bottom and increased the bottom weight when the power input was maintained. Therefore, the pressure drop at 500 mm decreased to such a value that the current power input could not provide sufficient energy for F4 constituents to purify out of the column.

Overall, the column height increased the purity of citronellal in the F2 fraction while gradually decreasing its yield. However, the negative effect on citronellal content would appear if the column height surpassed the critical value (400 mm). In Figure 17a, the citronellal

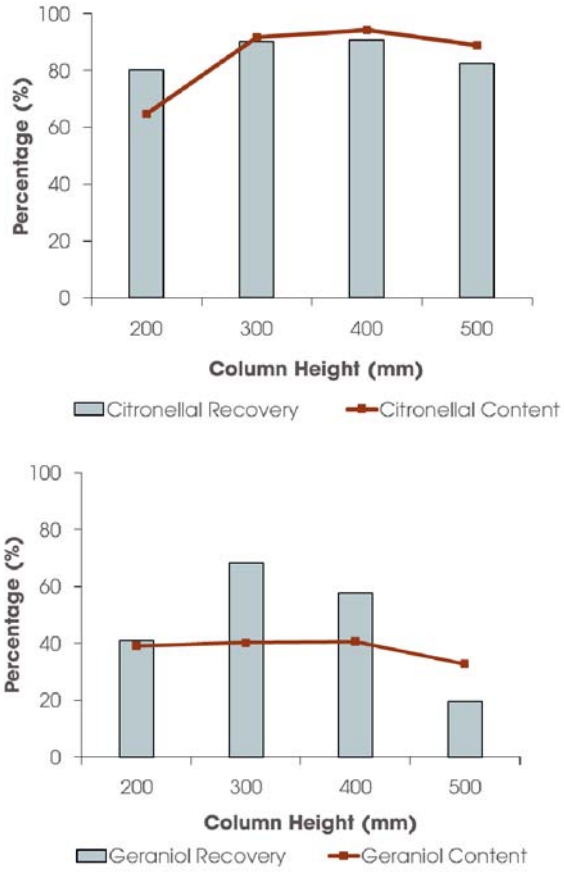


Figure 17. Effect of column height on the content and recovery of the key constituent (a) In F2 fraction, (b) In F4 fraction

recovery peaked at 300 and 400 mm, achieving almost the exact value of 90%. However, as the height of 400 mm allowed the highest citronellal content (94.33%), this height would be the most optimum height level of the fractionating column to purify citronellal.

For the F4 fraction, the geraniol purity increased slightly as the height level rose before considerably decreasing when the column height exceeded the critical value. Figure 17b illustrates that the geraniol recovery reached its peak at 300 mm (68.18%). However, the geraniol content was not the highest at this level, 40.26% compared to 40.61% at 400 mm. Meanwhile, the height level of 300 mm significantly increased the recovery, from 57.78% at 400 mm to 68.18% at 300 mm. As a result, the column height of 300 mm was selected as the appropriate column height to purify geraniol preliminarily.

Table 7 provides the composition pattern of each fraction when conducting the fractional distillation of CW oil under the optimum conditions. In summary, the fractional distillation at the optimum conditions allowed citronellal to experience an increase of 2.5 times in its content, from 37.68% to 94.33%. Meanwhile, geraniol purity reached 40.61% in the F4 fraction from an initial content of 17.33% in the raw CW oil. For the F3 and bottom fraction, a small amount of geraniol was also presented, namely 21.63% and 4.20%. Hence, the geraniol recovery could still be improved in further studies. Besides, the bottom fraction mostly consisted of high boiling point sesquiterpenes such as γ-muurolene (1.93%), germacrene D (5.84%) and α-muurolene (5.45%).

Table 7. Composition of each fraction in the optimum fractionation of citronella oil

[a]RT	Compound	GC-MS Percentage Area (%)					
		[b]Raw	F1	F2	F3	F4	B
8.47	limonene	4.21	28.02	0.11	[c]–	–	–
9.55	linalool	0.83	4.39	1.82	0.10	–	–
10.40	*β*-citronellal	37.68	61.81	94.33	5.58	0.36	0.31
10.59	isopulegol	0.51	0.99	–	0.45	–	–
11.50	citronellol	10.01	0.91	0.73	33.26	24.56	0.41
11.77	neral	0.34	0.47	–	1.87	0.39	0.06
11.91	geraniol	17.33	0.61	0.71	21.63	40.61	4.20
12.17	geranial	0.64	–	–	2.50	1.27	0.17
13.26	citronellyl acetate	3.71	–	–	8.24	9.61	6.09
13.45	eugenol	0.99	–	–	0.61	0.65	0.85
13.67	geranyl acetate	4.14	–	–	2.58	6.66	8.02
14.00	*β*-elemene	3.18	–	–	16.51	8.40	0.56
14.42	*β*-ylangene	–	–	–	1.19	0.35	0.62
14.55	*β*-gurjunene	–	–	–	0.45	0.29	0.32
14.75	*cis*-Muurola- 4,(14),5- diene	–	–	–	0.12	0.15	0.15
15.11	*γ*-muurolene	–	–	–	0.55	0.95	1.93
15.24	germacrene D	3.40	–	–	0.68	2.09	5.84
15.41	*α*-muurolene	1.40	–	–	0.24	0.92	5.45
15.61	*γ*-cadinene	–	–	–	–	0.34	5.29
15.69	*δ*-cadinene	3.81	–	–	0.19	1.47	16.38
16.00	*α*-elemol	3.38	–	–	–	–	19.77
16.41	globulol	0.57	–	–	–	–	0.81
16.68	6-*epi*-shyobunol	–	–	–	–	–	0.83
17.05	*epi*-*γ*-eudesmol	–	–	–	–	–	2.65
17.14	*τ*-cadinol	0.85	–	–	–	–	5.58
17.30	*α*-cadinol	–	–	–	–	–	8.87
Total		96.99	97.20	97.70	–	99.09	95.16

[a]Retention time (min); [b]Raw citronella oil; [c]Not detected

CONCLUSION

In this paper, the optimum conditions and the effect of three vital variables were investigated on the fractional distillation of citronella (*Cymbopogon winterianus*) oil, namely system pressure, packing types, and column height. The optimum conditions for citronellal would be the 400-mm Hempel column filled with large Fenske helices at 60 mmHg. For geraniol, a 300-mm Hempel column packed with Fenske spiral prismatic at 20 mmHg was the greatest condition. Owing to the distillation, citronellal experienced an increase from 37.68% to 94.33%. Meanwhile, geraniol purity reached 40.61% from 17.33%. Overall, the recovery was up to 90.00% with citronellal and 68.18% with geraniol. The fractionation of citronella oil may provide a huge profit since it could produce up to two of the preferable constituents, citronellal and geraniol. The distillation technique expressed an impressive efficiency regarding citronellal isolation while inferior with geraniol. The relatively close boiling point between geraniol, citronellol, and their esters prevented an effective separation. Hence, fractional distillation would be a potential method for obtaining high-purity citronellal and refining geraniol preliminarily.

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