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Research on Distillation Technology to Extract Essential Oil from Melaleuca Alterfornia (TTO)

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Abstract. Tea tree oil (TTO) comes from the leaves of *Melaleuca alternifornia* that belongs to the myrtle family (Myrtaceae). It is one of the most powerful immune system stimulants and sorts out most viral, bacterial and fungal infections in a snap, while it is great to heal wounds and acnes. In Vietnam, *Melaleuca* trees can grow on acid land that stretches in a large portion of lands in the Mekong Delta region. So, there are some *Melaleuca* plantations developed under the Vietnamese government plans of increasing plantation forests now. The crude TTO was produced from the leaves and terminal branches of *Melaleuca* tree by steam distillation methods: using micro-wave, using outside boiler. The cleaned TTO with high concentration of terpinen-4-ol (over 95% v/v) was obtained by vacuum distillation process at different reflux ratios. The results showed that, in steam distillation process, the average productivity of crude TTO is among 2.37% (v/dry-wt) or 1.23% (v/wet-wt) and insignificantly changed with differences of raw material moisture, the vapour speed, also with different steam distillation methods. The optimal steam distillation time is 250 minutes. In vacuum distillation process, the optimal reflux ratio is R=2 and TTO product satisfied for pharmaceutical requirement. The purification of TTO meets International Standard ISO 4730. The results of this study are the basis for designing of TTO extraction systems on a large scale for industrial production.

Keywords: Essential oil, Extract, *Melaleuca alterfornia*, Steam distillation, Tea tree oil, Terpinen-4-ol, Vacuum distillation.

1. Introduction

Melaleuca alternifornia, is commonly known as Australian tea tree and *Melaleuca* tree, grows fast and can be harvested as early as six months. They have been used medicinally for centuries by Australian aboriginal people. Tea tree oil (TTO) that comes from their leaves, contains over 100 components (mostly monoterpenes, sesquiterpenes and terpene alcohols) [1],[4],[5]. The studies demonstrated that terpinen-4-ol, a monoterpene is the most abundant (minimum 30%) and responsible for most of the antimicrobial activity, besides TTO also contains various amounts of 1,8-cineole that causes skin irritant[1],[5]. In an agriculture-based country like Vietnam, the acid land is actually not used for cultivation except for *Melaleuca* trees. So develop techniques to extract and refine essential oil from *Melaleuca alternifornia* leaves and research its cosmetic applications will improve the living standard of families in the area, especially for the farmers living on acid land.

Most essential oils available today are extracted by steam distillation among, although there are various extraction methods such as distillation, CO_2 supercritical extraction, and solvent extraction. It's the oldest form of essential oil extraction, quite simple and the best method for distilling leafy materials. Moreover, this process not only causes minimum changes to the essential oil composition during extraction, but also the steam is readily available, cheap, not hazardous and can be recycled. So steam distillation is used to collect crude TTO (35 – 45% of volume of Terpinen-4-ol) [2].

After steam distillation, the commercial value of TTO is not high, so it should be refined to increase its commercial value and fit with tea tree oil standard. Some refinement methods are vacuum distillation, crystallization, chromatography column… In this experiment, we focus on vacuum distillation to decrease TTO boiling point, thus limiting degradation of heat-sensitive volatiles.

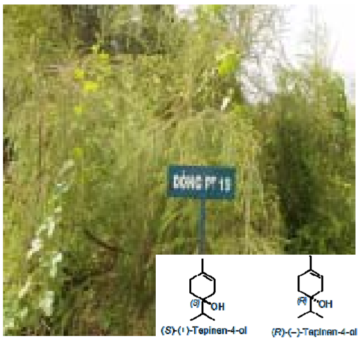

Fig. 1: Melaleuca Tree in Vietnam and two isomers (S) and (R) of terpinen-4-ol

2. Materials and Methods

2.1. Essential Oil Extraction – Steam Distillation Process [2]

In this experiment, TTO were produced by steam distillation from the leaves and terminal branches of Australian *Melaleuca* trees that were planted in Tan Phuoc District - Tien Giang Province – Vietnam (*Figure 1*). Dry materials were obtained after 24 hours of drying, and then determined the moisture of these materials (representative sampling). We distilled both dry and wet materials to exam impact of moisture in raw materials to essential oil amount extracted.

In the laboratory scale, we studied steam distillation methods: using micro-wave, and outside boiler. The main device for this process is distillation vessel of which dimensions are 1110mm diameter, 1689mm height. The operation parameters of this one are 120^{o}C and 2 bars in 3 hours. Besides, steam distillation process was also carried out on standard equipment according to standard of Vietnamese pharmacopoeia equipment. For steam distillation process using outside boiler, steam capacity is about 350 kg water per hour. The steam flow rate into distillation vessel is adjusted automatically by controller connected to the temperature sensor and the pressure sensor.

Mixture from condenser includes water and essential oil. Because of the difference of their specific gravity, they will become two liquid phases in the separator. The amount of essential oil that dissolved in the distillate water is small (negligible) and therefore recovery of essential oil dissolved in the water is unnecessary.

2.2. Essential Oil Refinement – Vacuum Distillation Process [2]

Crude TTO (35 – 45% of volume of terpinen-4-ol) from steam distillation process were used as materials for this study. In pilot scale, the parameters of distilling equipment are 5cm inside diameter and 1.5m long column which is filled by mesh buffer materials (*Figure 2*).

First, feed the crude essential oils into the reboiler of the vacuum distillation column. Then, the feeds are boiled by indirect heating resistor via thermal oil heater. A vacuum generator is connected to the top of distillation tower to create low-pressure in system. In front of the vacuum generator, we put the liquid separator, which is cooled by liquid nitrogen, in order to condense completely essential oil entrained by the vacuum line and to protect this engine.

The reflux ratio (R) was set by adjusting On/Off time of solenoid valve to take TTO out. When the valve closes (timer OFF), TTO vapour was condensed at the top of the tower and made a reflux stream back to the tower. Conversely, when the valve opens (timer ON), TTO vapour was brought to condenser. Because On/Off cycle is very short (in a few seconds), it can be considered as continuous circulation process. Two thermometers are put on the bottom and top of distillation column to determine each interval exactly.

The purpose of TTO purification is to create product that has low concentration of 1,8-cineole and high concentration of terpinen-4-ol. In this experiment, we carried out in conditions: 6000ml of feed volume, 5mmHg and reflux ratios (part returned condensate to part condensate take off) was changed from 1 to 3.

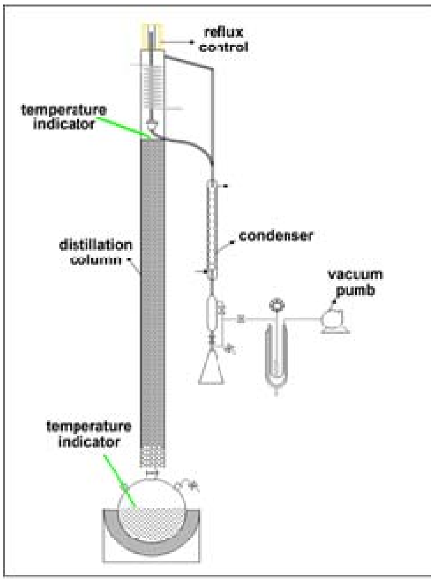

Fig. 2: The vacuum distillation system

2.3. Component analysis of TTO products

The GC used in this analysis was an Agilent 6890N with a flame ionization detector. Separation took place in DB-5 column (0.32mm x 30m x 0.25µm), using nitrogen as carrier gas. The GC oven temperature was initially controlled at 50^{o}C, then it was increased at a rate of 5^{o}C per min to 80^{o}C which was held for 1min, finally it was increased at a rate of 20^{o}C per min to a final temperature 220^{o}C which was held for 10 min.

3. Results and Discussions

3.1. Steam distillation process

For extraction by the standard steam distillation equipment, we carried out five batches to determine average productivity of TTO (*Table 1*) and the influence of raw material moisture. The results showed that, the essential oil percentage lightly decreased after several days, so the raw material can be oil extracted from fresh or drier.

Table 1: The productivity of TTO by the standard steam distillation equipment

Batch	Raw material input (g)	Moisture (%)	Vapour speed (g/h)	Time extract (minutes)	Oil volume (ml)	Productivity* % (ml/100g)	Note
1	100	48.2	180	245	1.3	**2.51**	Fresh (1)
2	100	32.31	180	240	1.7	**2.51**	After a day (2)
3	100	10.5	180	235	2.2	**2.45**	after12 days (3)
4	100	42.4	180	250	2.1	**3.64**	fresh leaves (4)
5	100	9.05	180	300	3.2	**3.59**	leaves after 30 days (5)

(1), (2), (3): materials are leaves and small brands.

(4), (5): fresh leaves without brands.

*: productivity is quantity of essential oil (ml) per 100g of dry materials

Table 2 shows the results for laboratory micro-wave steam distillation, the essential oil percentage lightly increased after two days.

For steam distillation using outside boiler, we carried out five batches to determine average productivity of TTO. The results were described in *Table 3*. The essential oil percentages not much change when keeping long time extraction, so just keep enough time for extraction. Water loss (energy loss) for extraction is 125-

180 (ml water loss /ml essential oil), so less energy is more time and contrariness. The yield of the steam distillation process was insignificantly changed with different distillation methods, also differences of raw material moisture. In another way, we can reduce energy loss by dry material to move away moisture as batch 5.

Table 2: The productivity of TTO by the laboratory micro-wave steam distillation

Batch	Raw material input (g)	Moisture (%)	Microwave Power (W)	Time extract (minutes)	Oil volume (ml)	Productivity* % (ml/100g)	Note
1	100	45.2	800	30	1.3	**2.38**	Fresh
2	100	30.3	800	30	1.7	**2.44**	After 2 days

* : productivity is quantity of essential oil (ml) per 100g of dry materials

Table 3: The productivity of TTO by the steam distillation in the pilot scale.

Batch	Raw material input (g)	Moisture (%)	Real dry Material (g)	Vapour speed (g/h)	Time extract (minutes)	Oil volume (ml)	Productivity* % (ml/100g)
1	4000	48.32	2067	1000	360	48	**2.32**
2	4000	47.74	2090	2000	220	47	**2.24**
3	4000	32.61	2696	2500	260	61	**2.26**
4	4000	23.55	3058	3000	250	71	**2.32**
5	4000	10.06	3598	4000	220	82	**2.28**

* : productivity is quantity of essential oil (ml) per 100g of dry materials

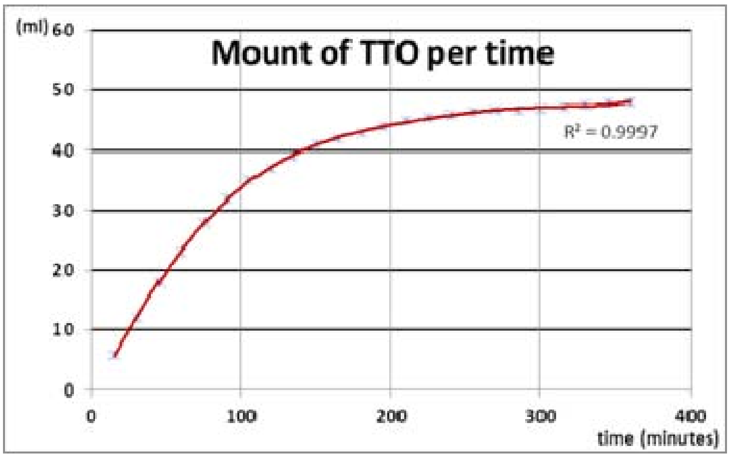

Fig. 3: Mount of essential oil per time.

Despite of the different moisture and speed steam, the productivities are nearly equal. The essential oil extraction speed is the highest at start and slows down in time (*Figure 3*). The results showed that, amount of oil recovery rapidly increased in the first 100 minutes of the extraction process, and terminated in around 250 minutes.

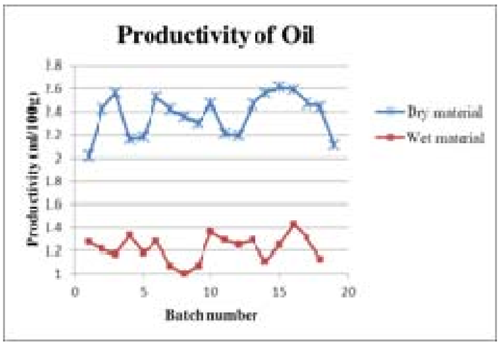

Fig. 4: Crude TTO productivity for dry materials and wet materials.

Table 4: Component of steam-extracted TTO before purification.

Component	% Concentration (v/v)
α-pinen	1.96 - 2.72
Terpinen-4-ol	31.8 - 47.02
α-terpinen	8.65 - 9.04
Limonen	3.49 - 4.68
p-cymen	1.56 - 7.215
1,8-cineol	4.44 - 7.141
γ-terpinen	16.747- 19.20
Terpinolen	5.58-13.71
α-terpineol	2.79-3.32

The yield of essential oil is typically 1 to 2% of wet material weight [1]. In this study, the average productivity is among 2.37% (v/dry-wt) or 1.23% (v/wet-wt), *Figure 4*. With *Melaleuca* trees in Tien Giang province – Vietnam, the results are also consistent with some studies in other provinces of Vietnam (Long An, Can Tho, An Giang…).

According to *Table 4*, two significant components of TTO after steam distillation meet International Standard ISO 4730 (terpinen-4-ol > 30% and 1,8-cineol < 15%). However, we still continued refining crude TTO and compared the benefits between crude TTO production and cleaned TTO production in order to determine the TTO type that we will apply in industrial scale.

3.2. Vacuum distillation process

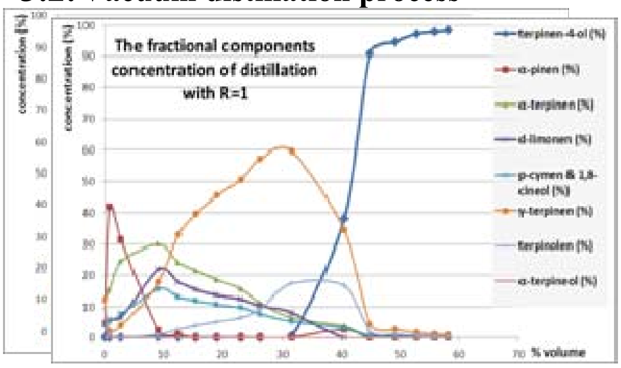

Fig. 5: The fractional components concentration of distillation with R=1.

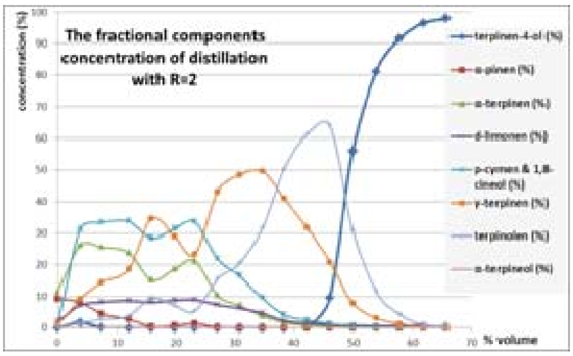

Fig. 6: The fractional components concentration of distillation with R=2.

Fig. 7: The fractional components concentration of distillation with R=3.The results of vacuum distillation process are shown in *Figure 5*, *6*, and *7* with differences of reflux ratios that changed from 1 to 3, respectively. The concentration of terpinent-4-ol was different in intervals. For vacuum distillation process, when increasing the reflux ratio, the high terpinent-4-ol concentration would be increased. However, increasing the reflux ratio will lead the high energy consumption of the process. The optimal reflux ratio of R=2 has been chosen and TTO product satisfied for pharmaceutical requirement in this case.

4. Conclusion

Research on purification of TTO had been carried out via two steps: steam distillation (essential oil extraction) and vacuum distillation (essential oil refinement). The results showed that, the productivity of TTO not much changes with differences of raw material moisture, the vapour speed, also with different steam distillation methods. The average productivity is among 2.37% (v/dry-wt) or 1.23% (v/wet-wt) with the optimal distillation time is 250 minutes.

In vacuum distillation process, the optimal reflux ratio in this study is R = 2, terpinent-4-ol was obtained in last fractionation of the vacuum distillation (from 45 – 67 % volume). The results of this study are the basis for designing of extraction systems of TTO on a large scale for industrial production.

5. Acknowledgement

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6. References

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