The Recovery of Parsley Seed Oil

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Commercial recovery of essential oils following steam distillation normally relies on the separation of the oil from water into a discrete phase and accumulation of the oil in traps. Observations from a local commercial process have confirmed that, while the essential oil of parsley seed adequately forms a separate phase from the water, it may separate further into floating (top) and sinking (bottom) fractions. This confirms literature reports of Akhtar et al. and Ashraf et al.[1,2] In the Ashraf study, 26% of the oil sank. Although the specific gravity of the oil was close to that of water (0.995), this may not be the only reason for significant fractionation into top and bottom oils. In the Akhtar study, a recoverable amount of bottom oil separated out despite a considerably lower specific gravity (0.915) than water. Guenther quotes specific gravities of 1.043-1.110 for parsley seed oil and 0.902-1.016 for herb oil, the specific gravity increasing as seed sets and matures.[3]

Fractionation into top and bottom oils complicates recovery—traps for both fractions must operate efficiently. The omission of either trap or incorrect operation could lead to significant losses during the recovery stage. The frequency, extent and main factors of fractionation are not well documented in the literature although a local processor suggests that the temperature of the distillate during the condensation and separation processes has a significant influence on the recovery and quality of the oil.[5]

The work reported here was designed to determine which factors affected the fractionation to top and bottom oil, and to make suggestions on how oil recovery could be improved.

Materials and Methods

Seed was harvested from a local crop of plain leaf parsley (Petroselinum crispum). Seed samples (25 kg) were steam distilled for 5 hours. The steam with entrained oil was passed through a water-cooled condenser. The condensate was passed through a heat exchanger coil before passing through traps designed to separate and recover the top and bottom oil. The arrangement is shown in figure 1. The temperature of the condenser was regulated independently of that of the coil and traps. The traps were insulated and were kept within 2°C of the coil by the flow of condensate.

The composition of the oil was analysed by gas chromatography, using the following operating conditions:

> Column—glass 5% SP2100/0.1% SP401, 1.8m x 6mm
> Temperature programme—70° to 122°C at 4°/m, then to 210°C at 8°/min
> Injection and detector temperature—250°C
> Carrier gas—nitrogen, 30 ml/min

Results are expressed as percent of component in the oil, uncorrected for detector response. Identification of individual components are based on GC-MS data. The major components (95%+ of the oil) fall into two clearly defined groups:

—Monoterpene hydrocarbons (MHC): α-pinene, myrcene and β-phellandrene.
—Allylbenzene derivatives (ABD): myristicin, apiole and 2,3,4,5-tetra-methoxybenzene (TMAB).

Figure 1. Diagram of Arrangement of Distillation and Separation Apparatus (not to scale)
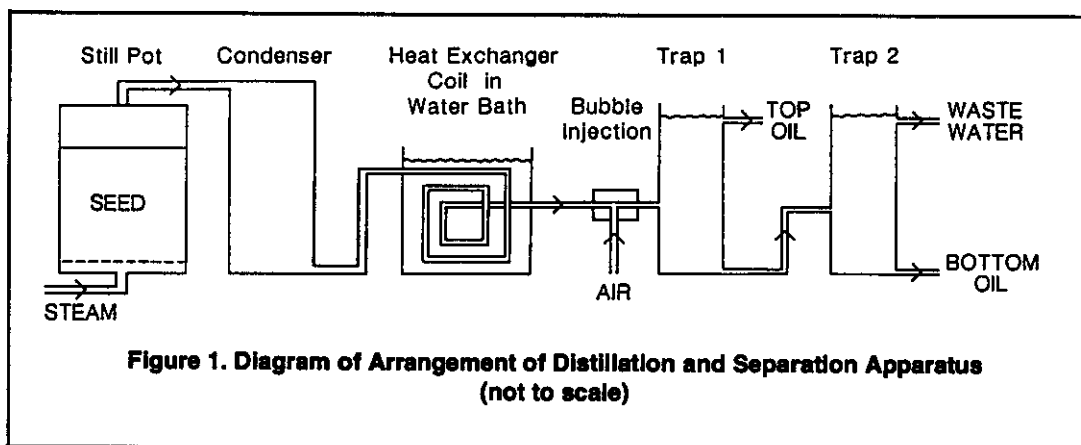
Densities were measured at 20° using specific gravity bottles.

Solubilities of oil in water were determined by stirring 100 ml of oil in 1 liter of distilled water at 20° and 45°C for 3 hours. The oil and water were stirred gently with a mechanical stirrer so that most of the oil was in droplet form but was not emulsified.

Least significant differences (LSD) are shown for p = 0.05.

Experiment 1—temperature variation during oil recovery. Duplicate distillations were done using the temperature (°C) settings shown in Table I. The coil and traps were adjusted to the required temperature before starting the 5 hour

Table I

Setting	Condenser	Heat Exchange Coil	Traps
1	15	15	15
2	45	45	45
3	15	45	45
4	45	15	15

extraction. Top oil was run off frequently enough to prevent accumulation and sinking (see below). After each run, the bottom oil was removed from the trap. Both oil fractions were allowed to stand overnight before final separation from water. No solvents were used to achieve separation. Air bubbling was eliminated as much as possible.

Experiment 2—oil fractionation by air bubbles. During preliminary distillations, air became entrained as bubbles in the distillate stream and rose to the surface in the first trap (to recover top oil). Observation of the bubble movement revealed quite clearly that a considerable amount of oil was carried on the underside of each bubble. Very few oil droplets rose to the surface independently of the air bubbles. Those that did appeared to be associated with turbulence in the trap. Any oil that surfaced immediately accumu-

lated in a thin film by surface tension. When the weight of accumulated oil exceeded a critical value, large globules of oil detached themselves from the surface layer and sank rapidly to the bottom. Duplicate distillations were carried out at temperature settings 1 and 2 in Experiment 1 (Table I), under the aeration regimes in Table II.

Table II

Time (minutes)	Aeration
0 - 30	None - stabilization period - no oil collected
30 - 90	None - first oil collected
90 - 150	Fine - bubbles <1 mm diameter
150 - 210	Coarse - bubbles 6-8 mm diameter
210 - 270	None - last sample collected

Air bubbles made up 5-10% (fine) and 20-25% (coarse) by volume of the distillate stream. The bubbles were introduced immediately before the first trap (see figure 1). The oil from each of the four regimes was collected and stored separately, as in Experiment 1.

Results

The temperature of the condenser and that of the coil and traps were varied to determine their effects on oil recovery, fractionation and composition. The results are summarised in Tables III and IV.

Table III. Essential Oil Recovery and Fractionation Following Separation at Different Temperatures

Run	Condenser (°C)	Coil/Traps (°C)	Total oil (g)	Top oil (%)
a	15	15	316	2.5
b	45	45	321	0.0
c	15	45	291	0.7
d	45	15	312	2.2
LSD			29.1	3.9

Table IV. Composition of Oil Fractions Recovered Following Separation at Different Temperatures (peak area %)

| | Condenser/coil and trap temperatures (°C) | | | | | | | | |
| | 15/15 | | 45/45 | | 15/45 | | 45/15 | | |
	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	LSD
alpha-Pinene	13.9	8.9	11.1	-	14.6	7.5	14.3	5.8	5.4
Myrcene	11.4	9.0	9.7	-	12.0	8.2	12.0	7.3	3.5
beta-Phellandrene	7.6	7.2	6.7	-	7.9	6.6	7.8	6.2	2.0
Myristicin	35.0	39.3	37.5	-	33.9	39.7	34.2	40.7	4.1
TMAB	14.4	15.4	15.4	-	14.1	16.5	14.0	17.2	3.0
Apiole	15.2	17.5	17.1	-	14.6	18.4	14.9	19.6	3.5
Total MHC	32.9	25.1	27.5	-	34.5	22.3	34.1	19.3	10.7
Total ABD	64.6	72.2	70.0	-	62.6	74.6	63.1	77.5	10.2

Operating temperatures had no significant effect on total oil extracted or fractionation into top and bottom oils. Further, no significant changes could be induced by changing these temperatures. Despite precautions, some air bubbling occurred as the first distillate of the first and last runs came through the coil. The slightly higher percentage of top oil collected in these runs is ascribed to the air bubbling.

Analysis of the oils which had separated during overnight contact with water showed a consistent trend towards decreased MHC and increased ABD in the top oils.

In the second experiment, the presence of air bubbles and their size had significant effects on the extent of fractionation into top and bottom oils. The results are summarised in Table V.

The total oil recovered was not affected significantly by the presence or absence of aeration. Small air bubbles lifted a significant amount of oil to the surface. The larger bubbles lifted over half the oil emerging from the coil. The top and bottom fractions were finally separated from the water after standing overnight and analysed. The top fraction contained more ABD and less MHC than the bottom fraction.

To determine how these differences in composition may have arisen, further distillations were carried out in which the top and bottom oils were analysed immediately as they accumulated, and again when they had stood overnight in contact with water. The results are shown in Table VI.

When the top oil was analysed immediately, it did not appear to differ in composition from the bottom oil. After overnight contact with water, significant differences arose, confirming the results shown in Table IV. The specific gravities of the top and bottom oils were measured after overnight standing, as 1.119 and 1.080 (20°C) respectively. The top or floating oil had the higher specific gravity. Therefore, the fractionation cannot be explained as a natural floating off of a lighter oil fraction.

The differences in composition may have been due to differential solution of the individual oil components in the water. To test this, measurements were made of the solubility of the oil in water at 20° and 45°C.

Table V. Essential Oil Recovery with Different Degrees of Aeration during Separation (mean of 2 runs)

| | | 15°C | | | 45°C | | |
Sample	Aeration	Total	(g)	% Top Oil	Total	(g)	% Top Oil
1	None	79	(78)	0	76	(75)	0
2	Fine	58	(56)	9.4	51	(54)	18.6
3	Coarse	58	(54)	52.6	48	(51)	65.5
4	None	50	(49)	0	45	(47)	0
LSD		8.2	7.9	6.2	7.9	8.1	6.9

Note: Values in brackets indicate total oil recovered when aeration was excluded for the entire run.

Table VI. Composition of the Top and Bottom Oils after Separation at 45°C (mean of 2 runs) (peak area %)

	Immediate		Overnight		
	Bottom	Top	Bottom	Top	LSD
alpha-Pinene	14.8	14.9	14.3	6.2	1.0
Myrcene	12.5	12.7	11.8	8.1	2.3
beta-Phellandrene	8.8	8.5	7.7	6.8	1.8
Myristicin	32.7	33.4	34.5	39.7	3.1
TMAB	13.8	14.1	14.1	18.2	2.7
Apiole	12.0	12.3	12.9	16.9	7.5
Total MHC	36.1	36.1	33.8	21.1	1.6
Total ABD	58.5	59.8	61.5	74.8	4.5

Note: Immediate oil samples were removed for analysis immediately accumulation had started. Overnight separated oil and water were allowed to stand overnight (18 hours) before sampling for analysis.

Table VII. Composition of Oil after Washing with Water in Solubility Tests (mean of 3 runs) (peak area %)

		15°C		45°C		
	Original	Oil	Water	Oil	Water	LSD
alpha-Pinene	13.6	13.6	1.1	13.0	1.8	2.5
Myrcene	11.5	11.4	1.0	11.1	1.6	2.4
beta-Phellandrene	7.6	7.6	0.8	7.5	1.5	1.6
Myristicin	34.7	34.5	25.3	34.7	30.6	3.2
TMAB	14.0	14.1	35.6	14.2	28.0	4.9
Apiole	14.6	14.4	9.6	15.0	11.6	1.1
Total MHC	32.7	32.6	2.9	31.6	4.9	6.2
Total ABD	63.3	63.0	70.5	63.9	70.2	6.9

Note: Original values refer to the oil before coming in contact with the water. Oil values refer to the 100 mls of the oil after the test. Water values refer to the oil extracted with diethyl ether from the 1 litre of water.

As can be seen from Table VII, oil composition was not affected by water extraction—analyses of the oils after the solubility tests did not show any significant differences in composition. The solubility of the oil in water is low—0.03 and 0.07 g/l at 15° and 45°C respectively. The ABD appear to be more soluble than the MHC. Because solubility is so low, differential solubility does not appear to explain how the differences in composition arise in the top oil during overnight contact with water.

Discussion

Stahl and Jork, Ashraf et al. and Akhtar et al. have reported differing physicochemical data on essential oil from parsley seed. Our oil also differed markedly in composition from all these oils, having a more uniform distribution of the ABD.[1,2,6] It resembled the "mixed" race rather than any of the three races characterised by a predominance of one of the three reported by

Stahl and Jork. Our oil, with a mean specific gravity of 1.069 (30°C), falls within the range found by Stahl and Jork and is considerably heavier than the Pakistani oils (0.995 and 0.915 respectively). Its behavior differed in that it sank rapidly when the distillate water was free from turbulence and air bubbles.

Ashraf et al. and Akhtar et al. did not describe or measure the fractionation process. They did not make measurements of the separate oil fractions other than to report the fractions to have the same composition. Our results from separate measurements show that this is true immediately after fractionation, but that significant differences arise during overnight contact with the distillate water. The floating top oil becomes denser than the bottom oil (specific gravities of 1.12 and 1.08 respectively). This is accompanied by increases in the denser ABD and decreases in the lighter MHC.

The results do not suggest that fractionation by air bubbles selectively removes individual components to the top oil. The overnight change in composition does not appear to be due to the selective solubility of individual oil components in the distillate water, since extraction in water would give changes opposite to those observed.

Although the process by which these differences arise remains unclear, oil is in contact with distillate water for such a short time during the normal distillation process, that it seems unlikely that the process will significantly alter the composition of the oil. Our results strongly suggest that the oil should be removed as it accumulates, and not be left in contact with water for prolonged periods to "complete" the separation.

The results of the second experiment clearly

show that air bubbles can cause fractionation of an oil that would otherwise sink rapidly in non-turbulent water. Such fractionation has the effect of dispersing the oil throughout the distillate water and can prevent it from accumulating in one place, from where it can be removed for storage. As such dispersal becomes more extensive and persistent, there is a greater chance of oil passing through the trapping stage to waste, particularly if there is turbulence in the flow through the traps. If the specific gravity of the oil approaches that of water, the dispersal will tend to become more persistent as the oil sinks more slowly. To maximise recovery, the dispersal must be minimised and appropriate traps must be used.

It is essential that the range of specific gravity is known for each crop. Variations arising from cultivar must be expected.[6] The specific gravity of oil from parsley seed or herb from a crop with immature seed will be less than oil from fully mature seed.[3] As the specific gravity approaches 1, dispersal can be expected to become more extensive and persistent, and separation and accumulation slower or less complete. Since oils of significantly different specific gravities can be fractionated and dispersed, separate traps for both floating and sinking oils must be used to prevent significant losses. The use of both traps will also increase the versatility of the plant by increasing the range of oils that can be handled efficiently.

The waste water should be checked for oil which has been carried through the traps. Design of the condenser should allow reproducible regulation of the temperature of the distillate. The flow of the distillate into the condenser should be free of air bubbles. The trap design should eliminate turbulence in the flow, and allow sufficient time for the dispersed oil to separate and accumulate completely. The capacity of the traps must be matched to the maximum flow of the still. When an oil's specific gravity approaches 1, even well-designed traps may not prevent oil carryover. In such a case, some means of actively coalescing the oil droplets in the traps may be necessary, e.g., stainless steel mesh screens.[4]

While temperature did not appear to be a major factor in the partition and separation process in our study, it is regarded as important for the oil quality.[5] The only observed effect was to increase the solubility of the oil in water. Using the figures from our results and a local distillation process, losses of dissolved oil in waste water could be in the order of 27 and 64 g/hour at 15° and 45°C respectively, even if separation and accumulation of the oil phase were complete. Lower tem-

peratures would reduce this sort of loss which would be significant over a full day's operation, given the high prices obtainable for parsley oils. However, the density of the seed oil decreased more slowly than that of water as the temperature increased. For oils that are denser than water (specific gravity > 1), higher temperatures should help the oil sink more readily, so improving separation and accumulation. For oils with a specific gravity < 1, higher temperatures may encourage dispersion as the oil sinks more slowly.

Consequently, selection of operating temperatures will be a compromise that should be based on:

—careful observation of the performance of each distillation plant
—thorough knowledge of the physical properties of the oil from each crop
—a clear understanding of how temperature can specifically influence oil quality
—observations of how the behaviour of the oil changes with temperature
—the behaviour of the oil in the distillate stream and the efficiency of the trap(s) at any given temperature

Acknowledgements

References

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