

Comparison of Supercritical Fluid Extraction with Steam Distillation for the Extraction of Bay Oil from Bay (*Pimenta Racemosa*) Leaves

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Abstract: Bay oil, an extract of *Pimenta Racemosa*, is produced in Dominica by the traditional process of Steam Distillation Extraction (SDE), and commercially utilised in the perfume and food industries. The objective of the work described in this paper seeks to investigate if it could be better produced by Supercritical Fluid Extraction (SFE) using carbon dioxide as extracting fluid. Experiments were therefore carried out on a bench scale SFE unit to evaluate the extraction characteristics of bay leaves and to compare the results with those from a bench scale SDE unit. The results showed that the SFE extracts contained mainly eugenol and chavicol up to about 1 hour of extraction time, after which higher components, including waxes, were incorporated into the extracts. The optimum operating conditions were deemed to be 150 bar pressure and 50°C temperature. The SDE extracts were also mainly eugenol and chavicol, but in addition contained a significant quantity of myrcene. The extract yield from SFE after 1 hour was similar to that of the ultimate yield from SDE (~4.0%), but the extraction time for SDE was in excess of twice that figure. It is concluded that the higher phenol content of the SFE product together with lower extraction times makes the use of SFE potentially preferable to the traditional SDE process.

Key Word Index : Bay (*Pimenta Racemosa*) Leaves, Essential Oil, Steam Distillation, Supercritical Fluid Extraction

I. Introduction

Bay oil is the essential oil extracted from the leaf of the *Pimenta racemosa var racemosa* tree, a plant of the Myrtaceae family. The oil, traditionally obtained by various methods of distillation, is said to have a pleasant odour (1) and is used in the manufacture of perfumes and food flavourings. It is the major constituent of bay rum. In the wild the tropical evergreen tree can grow up to 15m, however commercially grown trees are not usually allowed to reach those heights being mostly restricted to 4m to facilitate harvesting and efficient management systems. The dominant global producer of bay oil is Dominica, mainly by farmers who have produced oil from their own small stills for the last century, but also more recently through a co-operative (Dominica Essential Oils Cooperative, DEOSCO) owned factory operating two steam distillation units.

Depending on the material used to make the still, the oil produced may have a yellow to dark brown colour, with the stainless steel stills producing the lightest coloured oils (1). The odour of the crude oil has been described as warm-spicy, strongly phenolic with a sweet-balsamic undertone (2). Its flavor has been described as warm-spicy, almost pungent with a somewhat bitter taste (3). Over 80 compounds have been identified in the oil, the major ones being myrcene, limonene, linalool, eugenol and chavicol (2), (4), (5). Evaluation of the quality of the oil is normally based on its phenol content, with oils containing 50 to 55% phenol being regarded as good quality, with those in the range 55 to 65% being regarded as the highest quality. Weiss (3) reported that the typical leaf oil content is commonly about 1.5-2.5% with the average yield from commercial distillers being around 2%.

The major objective of the study was to investigate the feasibility of replacing the traditional steam distillation process with that of SFE for the Dominica Essential Oils Co-operative. This was done by:

- 1) Evaluating the potential for extracting bay oil from bay leaves using SFE, and determining the effect of varying pressure and temperature on the yield and chemical composition of the bay oil
- 2) Comparing the results with those from extraction by the traditional Steam Distillation (SDE) process.

II. Materials and Methods

In order to minimize raw material variations, all leaves were obtained from a single tree located in a valley in the Northern Range in Trinidad in the Caribbean. A sample of the leaves was sent to the National Herbarium of Trinidad and Tobago for identification and vouchering where they were deemed to be *Pimenta Racemosa var. Racemosa*.

For the experimental programme, the leaves were first removed from the stems and stored in the laboratory under ambient conditions for about 3 days before extraction. This roughly simulated the commercial conditions, but also mitigated against excessive water hindering the SFE process. The moisture content of the leaves was measured by the official AOAC method 986.21 (Dean and Stark) for moisture in spices. The average moisture content of the leaves used in the experimental programme was measured to be ~25% w.b.

SFE Experiments: The main part of the experimental programme was carried out using an Applied Separations Spe-ed laboratory model Supercritical Fluid Extraction Unit with carbon dioxide as the extraction fluid. A 100ml extraction vessel was used throughout the experimental programme, the variables investigated being:

- Pressure - 100 to 300 bar
- Temperature - 32 to 70°C

All experiments were run for 4.5 hours and carried out in duplicate with the mass of extract measured and samples taken every 15 minutes for chemical analysis. Total oil extraction was determined as the mass of extract divided by that of the initial charge of leaves to the vessel.

Steam Distillation Experiments: Duplicate steam distillation extractions, which effectively acted as the control experiments for comparative purposes, were carried out on a standard Bench Scale unit utilising a charge of ~100gms

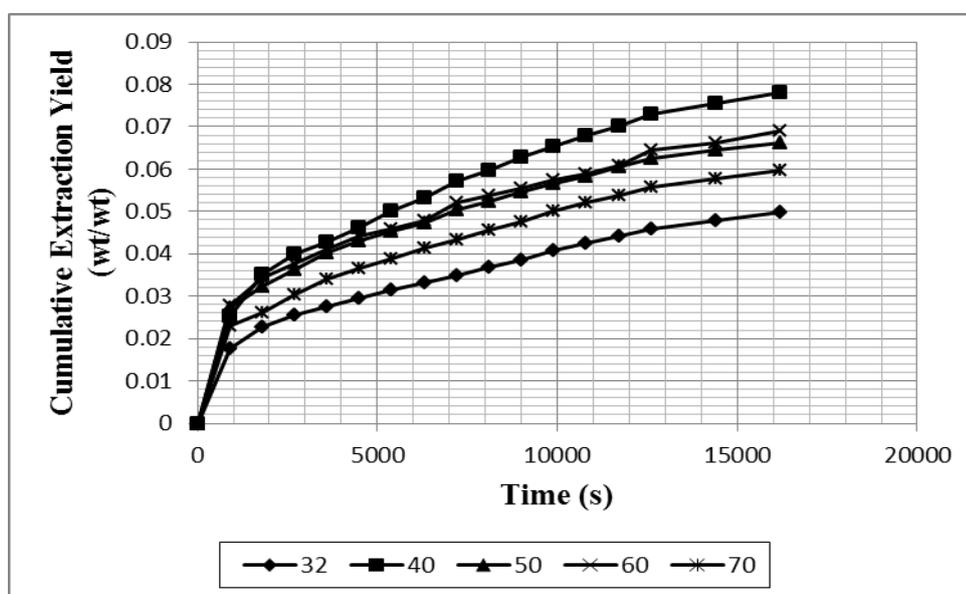
The experiments were run until extraction was complete i.e constant extract mass, with samples taken every 15 minutes for chemical analysis.

Oil Composition Measurements: Chromatographic analysis of the collected extracts was undertaken with the aim of identifying oil components and then quantifying the relative amounts of the major constituents as an indication of oil quality. Measurements were carried out using an Agilent Technologies 7890A GCMS with a 76838 Series injector. All peaks were identified and quantified, but five major peaks were identified. On the basis of the investigation of these major peaks, and having reference to the work reported in the literature, standards of myrcene, limonene, linalool, eugenol, and chavicol were sourced and utilized to further determine the relative amounts of these constituents.

III. Results and Discussion

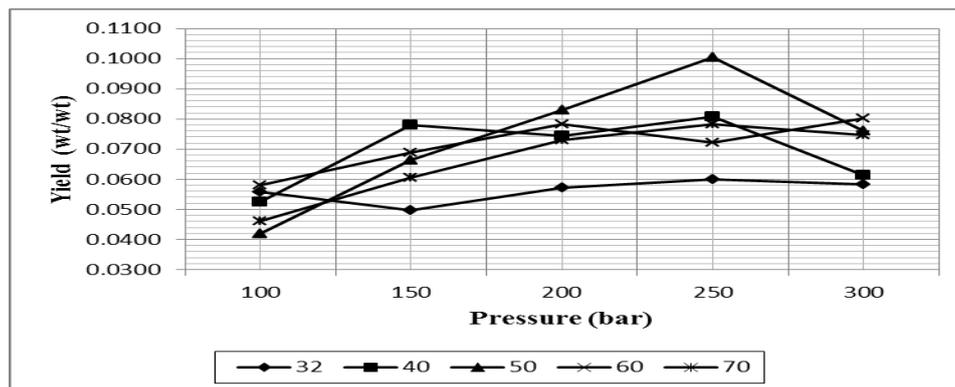
Supercritical Fluid Extraction Results: Typical extraction curves are shown in Figure 1, which shows the variation of yield with temperature at an operating pressure of 150 bar pressure. Reference to Figure 1 shows a sharp increase in extraction rates for the first half hour with a gradual falling off thereafter, but with some extraction continuing even after 4.5 hours.

Figure 1: Cumulative SFE Extraction Yield vs. time at 150bar and different Temperatures



The variation of final extraction yields with operating pressure and temperature are shown in Figure 2. The results indicate an increase in yield with pressure up to 250 bar operating pressure with a slight drop generally showing up when the pressure was increased to 300 bar.

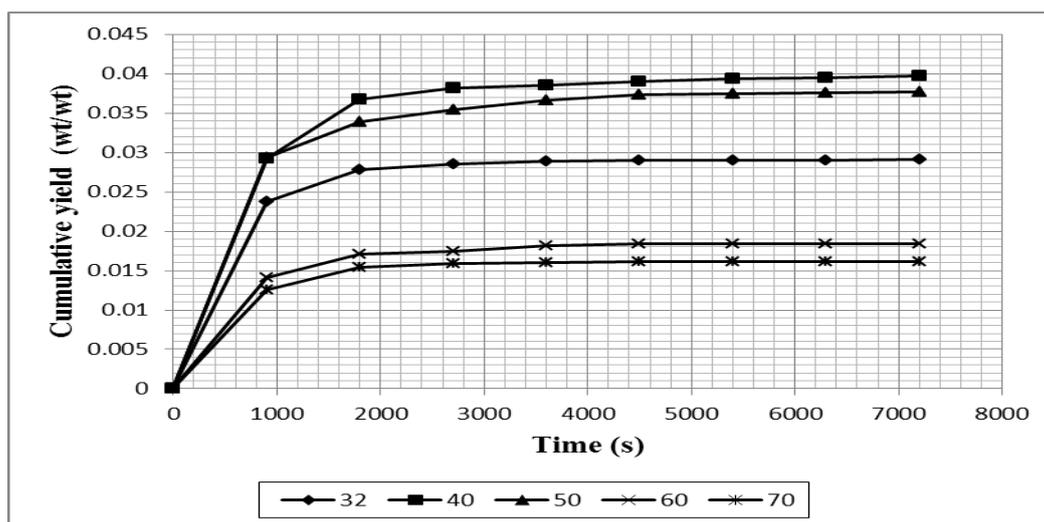
Figure 2: Variation of SFE Final Extraction Yield with Pressure



The results for varying temperature generally indicated lower yields at 32°C and 70°C, with similar yields in the range 40°C to 60°C.

When the cumulative yields of the key components (eugenol, chavicol, myrcene, limonene, linalool) are plotted against time as shown in Figure 3 however, it was seen that the bulk of the key components were extracted within the first hour of extraction. The effect of temperature is clearly seen in Figure 3 which shows similar yields at 40°C and 50°C, with a rather lower yield at 32°C and the lowest yields at the higher extraction temperatures. A similar effect was obtained at 200 bar operating pressure but with 50°C giving the slightly higher final yield also at ~4.0%. Although not shown in Figure 3, it is worth noting that the high total extraction yield of ~10% shown in Figure 2 at 250 bar operating pressure and 50°C temperature only gave a key component yield rather less than 4.0%.

Figure 3: Variation of key components yield with time at 150bar and different Temperatures



These results clearly show that for the operation of a commercial SFE process for bay oil extraction, the extraction should be stopped after a specific point in time to maximize the concentration of the quality components in the extract product. Continuing the extraction merely increases the extraction of the waxes and other higher components thereby reducing extract quality. This was confirmed by GC analysis where such components showed up on the chromatogram.

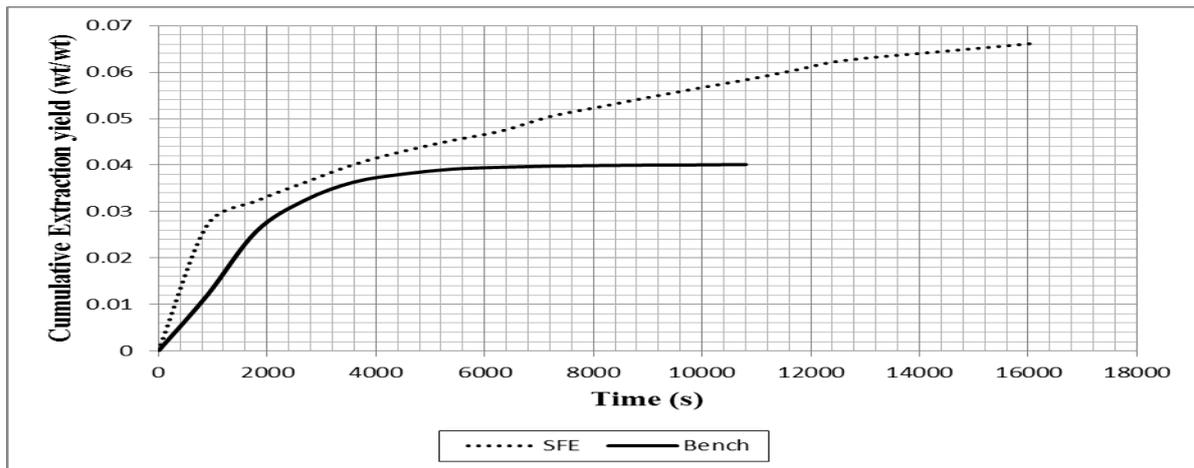
The results shown in Figure 3 seem to indicate that operating at 150 bar pressure and 40C temperature gave a higher yield of key components, based on initial charge than at 150 bar pressure and 50°C. However, reference to Table 1 shows that the actual composition of the key components in the extract at 50°C (>90%) was greater than that obtained at 40°C temperature. The optimum operating conditions were therefore chosen to be 150 bar pressure and 50°C temperature.

Table 1: Compositions of Key Components in Cumulative Extracts for the Different Extraction Methods

Compositions of Key Components in Extracts (wt. %)			
Components	SFE (150 bar, 40°C)	Bench Scale SDE	Optimum SFE Result (150 bar, 50°C)
myrcene	0.68	12.71	0.92
limonene	0.10	2.01	0.11
linalool	0.99	1.66	0.94
Eugenol	62.86	51.39	61.98
Chavicol	23.66	23.05	26.32
Total	88.29	90.82	90.27

Comparison with SDE: The basic objective of the investigation was to compare SFE with the traditional SDE process to evaluate whether there were benefits to replacing the technology on the commercial scale. In terms of comparing the basic extraction characteristics of the two technologies comparative extraction curves are shown in Figure 4 where the cumulative extraction yields are plotted against extraction time.

Figure 4: Cumulative Extraction Yield vs. Time for the different Extraction Methods



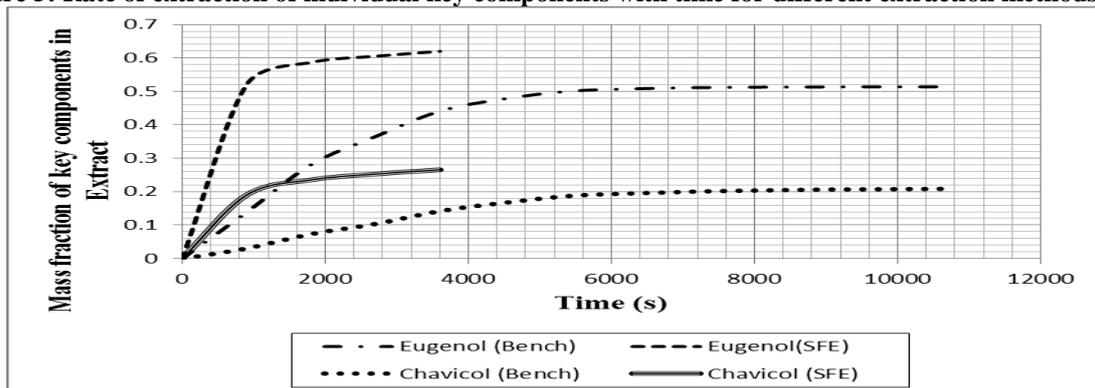
Reference to Figure 4 shows the SFE extraction to be faster than SDE extraction, but also the SFE extraction to be extended because of the additional extraction of the higher components using SFE after ~ 1 hour.

The comparison of the final cumulative extract compositions from SDE with that from SFE at the preferred conditions 150bar and 50°C, and under the conditions of highest yield i.e. 150bar 40°C is shown in Table 1.

In Table 1, the cumulative extract compositions for SDE are at the end of the experiments, whereas those for the SFE are after 1 hour.

When comparing the rate of extraction of the two major components with time, reference to Figure 5 shows SFE to extract the key components at a higher rate than SDE.

Figure 5: Rate of extraction of individual key components with time for different extraction methods



In comparing the compositions of the SDE and SFE extracts, reference to Table 1 and Figure 5 shows that whereas the oil components are similar, the SFE extracts after an hour of extraction time are mainly phenolic (~90%) with minimal myrcene, limonene and linalool. The SDE extracts however albeit with a high phenolic content, ~75%, have a significant myrcene content >10% with smaller amounts of the other two components. Using Guenther's (1) criteria for quality, the results show that SFE produces higher quality extracts. The lack of myrcene in the SFE extract may be due to its low solubility in CO₂ under the conditions used. In addition, myrcene decreases the oil's solubility in alcohol, but also readily polymerizes in the presence of air and light, so a significant myrcene content in the extract can imply a lower quality extract.

SFE can therefore produce an extract with very high phenol content, if the extraction is stopped at a specific time deemed to be about 1 hour with the bench scale unit. The yield is of the same order of that of SDE ~4.0%, but with the extraction time being roughly half of SDE.

IV. Conclusions

It may be concluded that:

- a) During SFE, the quality components are extracted in the first hour of the process, after which the extracts are increasingly contaminated with higher components and waxes
- b) Analysis of the initial extracts show that they are almost entirely of eugenol (~62%) and chavicol (26%), this implying that it is of high quality in terms of its commercial value.
- c) Optimum operating conditions were found to be 150 bar pressure and 50°C temperature
- d) The SDE extractions took longer to attain their ultimate yields than the SFE, and produced extracts which also contained myrcene (~12%) limonene (~2.0%) and linalool (~1.5%) in addition to eugenol (~50%) and chavicol (~20%)
- e) On the basis of the results obtained SFE is preferred to SDE because the phenolic content of the extract is higher and the extraction time is rather less.
- f) Replacement of the SDE with SFE will also allow for a greater operational flexibility in terms of its ability to produce a wider range of products from different agricultural materials.

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