A COMPARISON OF METHODS FOR THE EXTRACTION OF THE FRAGRANCE FROM YLANG YLANG

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Ylang Ylang is an essential oil traditionally extracted from the flowers of the tree *Canaga odorata.* It is used both in high-class perfumes as well as in basic toiletries e.g. soaps and shampoos, the traditional means of extraction being by steam/hydrodistillation. The major objective of the work described in this paper was to evaluate the potential for using Supercritical Fluid Extraction (SFE) with Carbon Dioxide, as an alternative to the traditional technique.

A bench scale SFE Extractor equipment was used in the experimental programme, the results being compared with those from steam distillation and hydrodistillation. The SFE programme also incorporated a study on the effect of flower maturity. Extraction performance was based on yield of oil, and chemical composition using Gas Chromatography.

Steam distillation tended to produce a product of the ‘floral water’ type, but hydrodistillation gave a clear oil with a yellow tinge, yields being up to 1.7% by weight. SFE was carried out over a range of temperatures varying from 100 to 400 bar (temperature 45^0C) and a range of temperatures varying from 35^0C to 75^0C (pressure 300 bar). These results showed yields generally to increase with pressure but with no significant temperature effect. Maximum yields were similar to those for hydrodistillation i.e. ~ 1.8%. Application of mass transfer theory showed that the bulk of resistance to mass transfer was external with calculated mass transfer coefficients being ~ $1x10^{-6}\ m^3m^{-2}s^{-1}$.

The chemical analyses of the two types of oil products showed some differences, with the oil from hydrodistillation showing slightly more of the quality defining esters such as benzyl acetate and benzl benzoate. The SFE products however showed relatively high percentages of eugenols (~24%). It is concluded that there is potential for the use of SFE technology in producing ylang ylang oils.

INTRODUCTION

The ylang ylang oil industry originated in the Philipines from as early as the mid eighteen hundreds where oil was extracted by either steam or hydrodistillation. Over the next century ylang ylang oil production spread westward to Reunion Island, then to Madagascar and the Comoro Islands, maintaining the same extraction techniques. These shifts were as a result of World Wars I and II, along with other regional and social changes. Over time however they have contributed to an overall decline in world production of ylang ylang oil. The lack of consistency in the ylang ylang oil industry, along with the fact that small distillers make up a large percentage of oil producers, have led to questions regarding the quality of ylang ylang oil now being produced. Its current main uses are in aromatherapy and fine perfumery.

This paper aims to compare the various extraction techniques that can be used to produce high quality ylang ylang oil. The bulk of the experimental work concentrated on evaluating the potential for using SFE with CO_2 as the extracting agent, these results being compared with those from bench scale steam distillation and hydrodistillation

MATERIALS AND METHODS

Raw Material and Sample Preparation

Flowers of the *Canaga odorata*, forma *genuina*, tree commonly referred to as ylang ylang were picked from trees cultivated on the hills of the Northern Range on the island of Trinidad in the Caribbean. The flowers were picked at 8 o'clock each morning and weighed before processing.

Flower Maturity Investigation

It was noticed during the initial stages of this investigation that ylang ylang flowers spent a period of 25-30 days on the tree, maturing all the while. Consequently an introductory investigation was undertaken to determine at which maturity stage the flowers should be picked in order to obtain the best quality ylang ylang oil. Traditionally, flowers were deemed ready for extraction when two red dots were observed at the base of each petal [1]. For this investigation five distinctive maturity stages were identified, three being described below:

Stage 1 where the flowers were least mature, the petals coloured milky green and showing no signs of red dots.

Stage 3 where the flowers were of moderate maturity, the petals coloured greenish-yellow to yellow and red dots visible.

Stage 5 where the flowers were of highest maturity, the petals limp and shrivelled and dark brown with no visible spots.

The ylang ylang oil was extracted using supercritical carbon dioxide on a bench-top scale Applied Separations (Penn. USA) Spe-ed SFE unit. A 100ml stainless steel extraction vessel packed with approximately 28g of flowers was used for each run and extraction conditions kept constant at 45^0C, 300 bars and 2.5L/min of expanded carbon dioxide gas. The collected oil samples were then analysed by gas chromatography (GC). Specific attention was paid to the components that were considered to be quality-defining components described in work done by Buccellato [2] on the odour and composition of ylang ylang oil. Previous work on ylang ylang flower maturity has been performed by Stashenko et al [3] where ylang ylang oil was extracted by simultaneous distillation and extraction using methylene chloride to capture the volatiles for analysis. In this work however only three maturity stages were identified.

Steam Distillation

The bench-top steam distillation apparatus used in this work comprised a heated 2L conical flask half-filled with water to generate steam, a bed of ylang ylang flowers contained in a vertical tube, condenser and separating funnel. A charge of 40g of ylang ylang flowers was used for each run, which lasted 3 hours. The oil-steam vapour was condensed and collected in a separating funnel for GC analysis.

Hydrodistillation

A Clavenger type apparatus was used to hydrodistill the ylang ylang oil. A mixture of approximately 1L water and 40g ylang ylang flowers was added to a 2L directly heated conical flask. The oil-steam mixture leaving the flask entered the condenser and refluxed for 3 hours. The resulting oil layer was quantified and collected for subsequent GC analysis.

Supercritical Fluid Extraction

The SFE of ylang ylang oil was performed on the same unit described in the maturity investigation. As before the 100ml extraction vessel was packed with approximately 28g of flowers. In these experiments, whilst the flower maturity and CO_2 flowrate were kept constant at Stage 3 and 2.5L/min respectively, the system pressure and temperature were varied. In the first series of runs the pressure was kept constant at 300 bars and the temperature varied from 35^0C to 75^0C in increments of 10^0C. In the second series of runs the system temperature was kept constant at 45^0C whilst the pressure was varied from 100 to 400 bars in 100 bar increments. SFE samples were collected and stored for subsequent GC analysis.

Gas Chromatography

The gas chromatography analysis was performed on a HP5890 Series II Chromatograph equipped with a hydrogen-air burning flame ionised detector (FID). The column used was a 60m Supelco SPB-50 column with an i.d. of 0.25mm, a coating thickness of 0.25µm and a bonded poly (50% diphenyl/50% dimethylsiloxane) phase. The oven temperature programme used was 75^0C to 250^0C at a rate of 5^0C/min and 30 minute hold at 250^0C. The injector temperature was set at 275^0C and the detector set at 300^0C. An injection volume of 1µL of the pre-diluted ylang ylang oil with 0.5ml of ethanol was used.

The peaks were identified by comparison with an external standard. An ylang ylang oil standard was prepared by mixing eight of the quality-defining components of ylang ylang. The standard was injected neat using a volume of 1µL.

Mathematical Modelling

The model used to correlate the results was based on an external mass transfer mechanism:

$$c(t) = c_s\,(1-\exp^{-ktA/V}) \qquad (1)$$

where, c(t) is fractional yield of extract at time, t (g/g), c_s is the final fractional yield of extract (g/g), A/V is the surface to volume ratio of the flowers (m^2/m^3) and k is the external mass transfer coefficient ($m^3m^{-2}s^{-1}$). A curve fitting technique was employed to fit the extraction curve predicted by the model to the experimentally determined extraction data, thereby yielding a value for the external mass transfer coefficient, k.

RESULTS AND DISCUSSION

The results from the GC analysis, shown in Table 1, compare favourable with previously mentioned work by Stashenko et al.[3], even though the oil extraction techniques were different. The components selected for this investigation were a mixture of esters, alcohols and phenols, the amounts of which varied with flower maturity. The trends identified by Stashenko et al. for the components considered were confirmed by this work, with only minor deviation for benzyl acetate and farnesol. Another startling deviation was the unusually high percentage of eugenol in the supercritically extracted oil, calculated to be twenty times that reported by Stashenko et al.. These deviations may be explained by differing climates, soils and growing conditions but the source of the eugenol anomaly hints strongly at the variation in extraction technique and associated efficiencies. Examination of the relative amounts of the quality-defining components leads to the selection of Grade 3 maturity flowers as those that yield ylang oil of the highest quality.

Steam distillation of Grade 3 maturity ylang ylang flowers produced a ‘floral water’ type emulsion instead of the distinct oil layer obtained by hydrodistillation. Consequently no quantification or analysis of the oil produced by steam distillation wa attempted. However, the yield of oil obtained by hydrodistillation was approximately 1.7%. GC analysis of the hydrodistilled oil showed it to be of comparable quality to other commercially available ylang ylang oils.

The extraction curves plotted from the SFE of ylang ylang experiments were of characteristic shape. The final yield increased with pressure to a maximum at 300 bars, shown in Figure 1. This conforms to accepted theory, which states that as the pressure increases so too does the solvent capacity [4]. Classic retrograde solubility behaviour described by Mukhopadhyay [5] was demonstrated in Figure 2 where the yield was seen to decrease with temperature at moderate pressures due to the density effect of the solvent. Additionally at the higher pressures the yields were observed to increase with temperature indicating that the system was well above the crossover pressure and the volatility effect of the solute was dominant.

The highest yield obtained with SFE at 1.8% was only slightly higher that that achieved with hydrodistillation. In addition to the yields being comparable so too was the quality of both oils. Although the hydrodistilled oil contained a higher percentage of benzyl acetate, the supercritically extracted oil was shown to possess equivalent amounts of the other esters, alcohols and phenols. Again an extremely high percentage of eugenol was observed in the supercritically extracted oil being ten fold the amount in the hydrodistilled oil. Taking into account both the quality and quantity of oil, the optimum extraction conditions for the SFE of ylang ylang oil were 300 bars and 45^0C.

The mathematical model, shown below, which was based on an external mass transfer mechanism shown in Equation (1) fitted well with experimental data. This served to help demonstrate the hypothesis that most of the oil was located on the surface of the petals with mass transfer being externally controlled. The values for the external mass transfer coefficient, k, were of the order of magnitude $10^{-6}m^3m^{-2}s^{-1}$, the variation with pressure and temperature being shown in Figures 3 and 4. Both plots show k increasing to a maximum value, which again conforms to established theory.

CONCLUSIONS

From the work reported in this paper it could be safely concluded that there is good potential for the use of SFE technology in the production of ylang ylang oil. Ignoring the effect of extraction technique, the use of Grade 3 maturity flowers was shown to yield the highest quality of ylang ylang oil. Both supercritical fluid extraction and hydrodistillation using a Clavenger type apparatus were shown to be superior techniques for the extraction of ylang ylang oil. The optimum conditions for the supercritical fluid extraction of ylang ylang were shown to be 300 bars and 45^0C, giving the highest yield and good quality. The external mass transfer equation was shown to adequately model the supercritical fluid extraction of ylang ylang oil giving values of k in the order of $10^{-6}m^3m^{-2}s^{-1}$.

NOMENCLATURE

$c(t)$ = fractional yield at time, t(g/g)

c_s = final fractional yield (g/g)
A/V = surface to volume ratio of the particles (m^2/m^3)
t = extraction time (s)
k = external mass transfer coefficient (m^3/m^2s)

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Table 1: GC Results for the Variation of Ylang Ylang Oil Composition with Flower Maturity from Mc Gaw et al. and Stashenko et al.

Component	Author	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Benzyl Acetate	Mc Gaw et al.	4.01	4.55	3.07	1.93	0.34
	Stashenko et al.	0.15	-	4.78	-	11.63
Benzyl Benzoate	Mc Gaw et al.	13.21	11.92	12.32	13.62	12.45
	Stashenko et al.	4.72	-	7.21	-	6.19
Eugenol	Mc Gaw et al.	21.28	21.58	21.92	20.40	20.17
	Stashenko et al.	0.25	-	1.03	-	0.37
Farnesol	Mc Gaw et al.	0.51	0.64	0.60	0.97	1.16
	Stashenko et al.	1.58	-	1.19	-	0.84
Geraniol	Mc Gaw et al.	0.02	0.02	0.04	0.02	0.03
	Stashenko et al.	-	-	-	-	-
Nerol	Mc Gaw et al.	1.31	1.39	1.39	1.38	1.73
	Stashenko et al.	0.00	-	0.10	-	0.27
Nerolidol	Mc Gaw et al.	0.00	0.61	0.06	0.05	0.09
	Stashenko et al.	0.00	-	0.17	-	0.13

For purposes of comparison Stashenko et al.'s maturity stages were, according to their description, classed as Stages 1, 3 and 5 using our maturity grading system.

Figure 1: Variation of Yield with Pressure at 45°C

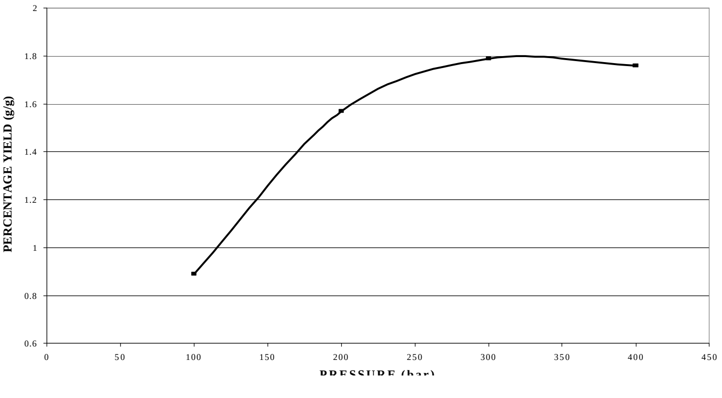

Figure 2: Variation of Yield with Temperature at 300 bars

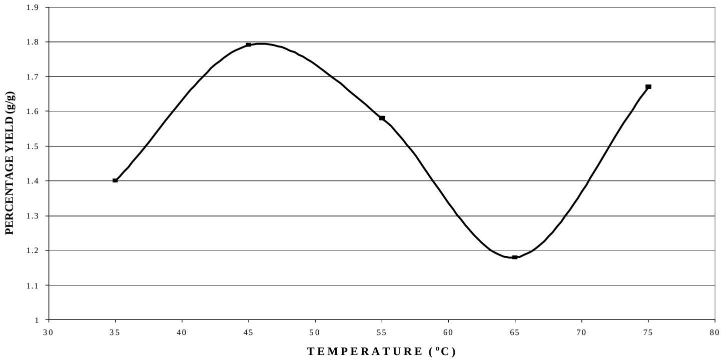

Figure 3: Variation of k with Pressure

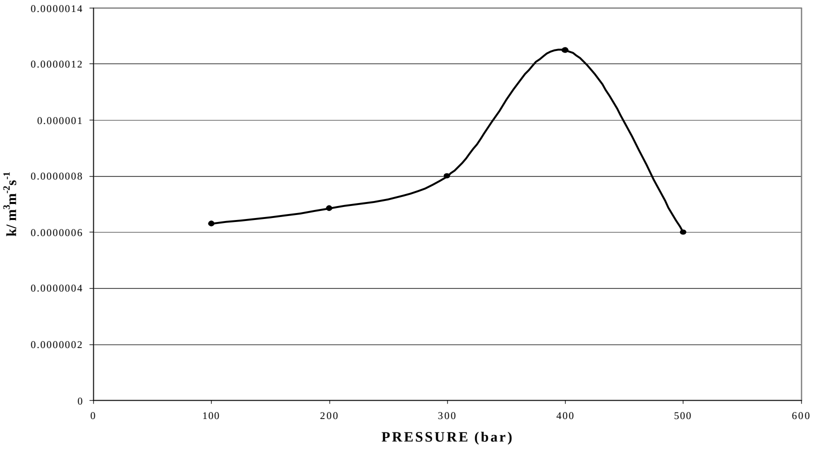

Figure 4: Variation of k with Temperature