

Processing of citronella oil, for commercial exploitation

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Abstract: The Java type Citronella oil is one of the most widely used perfumery oil. Because of its high Citronellal content (30 to 35%), and total alcohol as Geraniol (42 to 45%), its often used as a starting point for perfume materials, which are isolated or fractionated from the oil. In this paper various possible methods have been used to find out maximum yield of best quality of isolates and the economics of these fractions for the benefit of the farmers and new entrepreneurs.

(Keywords : Fractionation, Essential oils, Perfume, Fragrance, Flavour, Isolates)

Introduction

Citronella oil is one of the industrially important Essential oil obtained from different species of *Cymbopogon* belong to family Graminae. The essential oil is volatile oil produced by etc tm, or water distillation of whole plant. The vapours are condensed to yield a water condensate and oil that can be separated off, usually by gravity¹. It is classified in trade into two types: Ceylon citronella oil, which is extracted from *Cymbopogon nardus* and Java Citrinella oil, obtained from *Cymbopogon winterianus*. *Cymbopogon nardus* and *Cymbopogon winterianus* are both perennial grasses². These two species are distinguished from each other by different leaf morphology and chemical composition. The name Java Citronella and *Cymbopogon winterianus* was given to a variety of citronella for commemorating Mr. Winter, who was a pioneer oil distiller of Sri Lanka. The main difference between these two oils is the proportion of geraniol and eft, onellal. The java type oil generally is considered to be of superior quality to the Ceylon oil. The high proportion of Geraniol

and Citronellal in Java Citronella oil makes it an important source of various 'derivatives like Citronellol, Citronellyl nitrite and Hydroxycitronellal, which are extensively used in compounding high-grade perfumes³. The Ceylon type citronella oil, which contains relatively low Ciironellal, is mainly used as in cheaper products rather than for the production of derivatives. Fractionition is a process in which the oil is redistilled in vacuum so individual components, or fractions, are separated out as they evaporate one after the other. This is possible because fractions or constituent has its own rate of volatility based on time and temperature⁴. It's much easier for a perfume maker to create unique aromas by combining individual or combing whole oil with their complex mixtures of constituents. Citronellal and Geraniol are two most important and widely used perfume-designing materials⁵. Thus the aim of this study is to fractionate the oil into their various components and find out the economics of various valuable fractions⁶.

Material and Method

Java Citronelle oil of Assam region is collected locally and subjected to GC analysis by using Hewlett Packard 5890 series II gas chromatograph equipped with flame ionization detector (FID) and Carbowax 20nm polar fused silica capillary column (30m x 0.32mm.). The injector and detector temperature were maintained 21 Oc and 220 c, respectively. Nitrogen was used as carrier gas; flow rate 1.5 ml/min. The amount of sample injected was 0.1ml (split ratio 60:1). The oven temperature was programmed as 60-210c was programmed at 3c/min. After the analysis of Java Citronella oil, it was then separated into 'various fractions using a 5-litres capacity glass fractionating column equipped with 3-nech flask

capacity 5 litres, column 2"x4" with stainless steel wire sulzer packing, reflux divider 2", condenser 2"x24", receivers of 250ml, 500ml, 1000ml, tong with 300 liters per min. capacity vacuum pump. Glass reaction unit of 5 liters capacity fitted with Tenon stirrer, thermometer pocket and condenser and 250 ml capacity hydrogenation apparatus, shaker type Perfit Model were also used to carry out chemical conversion of fractions obtained from fractionation of oil into highly valuable components.

Java Citronella oil contains a number of fragrant fractions of which Citronellal, Geraniol, and Citronellol are the major components⁷. Gas chromatographic analysis of the Java variety indicates that the oil contains about 35% Citronella¹, 25% Geraniol, 3-4 % Geranyl acetate along with Citronellol 12% and Citronellyl acetate 3-4% contents. The chemical composition of Essential oil can vary tremendously. Other compounds predominant in citronella oil include beta Bourbonene, Elemol, L-borneol, and Nerol⁸. Fractional distillation of Citronella yielded 10 fractions that were tested commercially and economics of the oil was found out.

Processing of Java Citronella oil

Method -I

This was three-step method. Fractionation of oil for removal of the terpene and aldehyde under reduced pressure and the balanced portion of the oil is subjected to chemical conversion of the acetates into their corresponding alcohols⁹. There after the chemically treated or saponified oil is again charge into fractional distillation unit for the recovery of total alcohols and high boilers as elemol¹⁰. In this experiment 3kg material is taken for the purpose and results are shown in table-5.

Method —II

This was also three-step method¹¹. Fractionation of oil for removal of the terpene, aldehyde along with balanced part except residual part under reduced pressure and the balanced

portion of the oil is subjected to chemical conversion of the acetates into their corresponding alcohols¹². There after the chemically treated or saponified oil is again charge into fractional distillation unit for the recovery of total alcohol and high boilers as elemol. In this experiment 3kg material is taken for the purpose and the results are shown in table 6.

Economics of the valuable fractions

The economics is considered on the basis of the commercial scale processing charges i.e. average Rs 54 per kg of the oil for Citronellal, Geraniol and Rs 100 per kg for conversion of Citronellal into Citronellol. If the batch size is 180kg, the following values of the fractions were found. Rates of the oil collected from the Journal of Indian Perfumer, EOAI, New Delhi and cost of the products is shown in table-7.

Raw material cost

Cost of JCO @ Rs. 500 /kg	Rs. 90000.00
Misc. expenditure @ 5.0 % of total values of the oil	Rs. 4500.00
Processing charge @ Rs 55 /kg	Rs. 9900.00
Total cost	Rs. 104400.00

Hydrogenation of Citronellal

In the second step, the aldehyde Citronellal was hydrogenated in presence of activated Raney Nickel catalyst¹³. Whole Citronellal was converted into 95% Citronellol and 2-3% Dihydrocitronellol¹⁴. The converted Citronellal was then fractionated to recover Citronellal of 92% purity and yield was 90% of the total Citronellal¹⁵. The cost of hydrogenated Citronellol is given in table-8.

Economics of Hydrogenation process

Raw material cost

Total citronellal, = 63.0 kg	
Cost of citronella @ Rs. 750.00/kg = Rs 47250.00	
Processing charge @ Rs 100 per kg = Rs. 6300.00	
Total cost = Rs 47250.00+6300.00 = Rs.53550.00	

Total profit in processing including hydrogenation = Rs 12480.00 i.e. 11.95% of total raw material cost including processing charges and shown in table 9.

Results and Discussion

The composition of the oil that is used in the processing is shown in table-1. BIS specification and IS specification are also shown in table-2 and table-3. IS specification of Ceylon variety is also given for the comparison with .IC0 in table-4. The main components in processed JCO are Limonene 2.65%, Citronellal 32.12%, Citronellol 9.35%, Geraniol 24.47%, Citronellyl acetate 2.47%, Geranyl acetate 3.76%, Beta caryophyllene 1.8% and Elemol 4.58%. In the fractionation of the oil, various fractions were collected at required temperature and reduced pressure. These fractions were checked by Refractometer for knowing their respective Refractive index. Actually it is the quick and easy method of physical analysis during very sophisticated operation of fractionation unit. Vacuum was maintained 5-3mm and the processed temperature was maximum 165 °C. In the mean time these fractions sent for Gas Liquid Chromatography analysis for purity purpose. The recovery of the main products in both the method is given table -5 and 6. In the first method the recovery of the Geraniol is around 40% along with Elemol 7%. While in the second method the recovery of geraniol was up to maximum side 42% with Geraniol lower part 5%. The recovery of aldehyde Citronellal was almost same in both the methods. The hydrogenation of recovered Citronellal was carried out at specific pressure and temperature in presence of Raney nickel catalyst. The commercial grade hydrogen gas was added in the process. In the hydrogenation process

aldehyde citronellal of 90% purity was used. During the hydrogenation process the samples were collected at fix interval for seeing the conversion process whether it is going in forward direction with out formation of unrequired product and these unrequired product as Dihydrocitronellol should in less amount. According to the obtained results of processing of Java Citronella oil, the second method will be highly valuable for the commercial processing in which maximum recovery of Geraniol content with out formation of elemol. The major portion of Elemol gas into the residue. The Geraniol lower part in this recommended method is also behaves as geraniol oil: little inferior quality and it may use as cheapest fragrance material in the manufacturing of low cost perfume for Aggarbatti, Deepwatti. Economics of various fractions indicates that the processing of Java Citronella oil by using second method is more profitable than first method. The economic of the fractions is based on commercial processing charges that are accepted by the biggest essential oil and aroma chemical industries. The profit comes about 12% of per kg oil. Actually it is primary value addition of Java Citronella oil in which new entrepreneurs can entered easily for seeking primary benefit about 12% profit in the original oil. After that the secondary value addition is based on chemical reactions of the fractions obtained in the primary value addition of the oil. If the farmers or cultivators of essential bearing crops start this job, it may earn more profit than the trader.

Table-1: Quality parameters of citronella oil used in the processing.

Sr. No.	Quality parameters	Values
1	Refractive index at 27°C	1.4653
2	Specific gravity at 27°C	0.8823°C
3	Limonene	2.65%
4	Citronellal	32.12%
5	Beta caryophyllene	1.8%
6	Citronellyl acetate	2.47%
7	Geranyl acetate	3.76%
8	Citronellol	9.35%
9	Geraniol	24.47%
10	Elemol	4.58%

Table-2: BIS Standard for Java citronella Oil (IS : 512-1988)

Properties	Specifications
Colour and Appearance	Pale yellow to light tan clear liquid
Odour	Characteristic citrus grassy with rose undertone
Relatively density at 27°C	Minimum : 0.8743 Maximum : 0.8893
Refractive index	Minimum : 1.4624 Maximum : 1.4714
Optical Rotation	Range : -0.5° to -5°
Solubility in 80% (V/V) ethanol	One (1) Volume in two (2) volumes to give a clear solution
Total acetylizable matter calculated as geraniol, % by mass	85
Total Carbonyl compounds calculated as citronellal % by mass, Min	35-45
Mineral oil	No readal le separation of mineral oil
Steam distillation residue % by mass, Max	3

Table-3 : International standards for java citronella Oil (ISO 3848-1976)

Properties	Specifications
Appearance	Clear, mobile liquid
Colour	Pale yellow to pale brownish yellow
Relatively density at 20/20°C	Minimum : 0.880 & Maximum : 0.895
Refractive index at 20°C	Minimum : 1.4660 & Maximum : 1.4730
Optical Rotation at 20°C	Range : -5° to 0°
Miscibility in 80% (V/V) ethanol at 20°C	One (1) Volume in two (2) volumes to give a clear solution sometimes opalescence can be observed on continuing the addition of ethanol.
Ester value after acetylation	Minimum : 250- corresponding to 85% of constituents liable to acetylation, expressed as geraniol.
Carbonyl value	Minimum : 127 corresponding to 35% of carbonyl compounds, expressed as citronellal Minimum : 18- corresponding to 5% of carbonyl compounds, expressed as citronellal Maximum : 55- corresponding to 15% of carbonyl compounds expressed as citronellal

Table-4: International Standards for Ceylon citronella Oil (ISO 3849-1981)

Properties	Specifications
Appearance	Clear, mobile liquid
Colour	Pale yellow to pale brownish yellow
Relatively density at 20/20°C	Minimum : 0.894 & Maximum : 0.910
Optical Rotation at 20°C	Range : 20° to 12°
Miscibility in 80% (V/V) ethanol at 20°C	One (1) Volume in tow (2) volumes to give a clear solution
Ester value after Acetylation	Minimum : 157 & Maximum : 200
carbonyl value	Minimum : 18-corresponding to 5% of carbonyl compounds, expressed as citronellal Maximum : 55 corresponding to 15% of carbonyl compounds, expressed as citronellal

Table-5: Yield of various isolates in method-I

Sr. No.	Name of fractions (gm)	Wt. of fraction index n 20/D	Refractive GLC (%)	Purity by fractions (%)	Yield of
1	Limonene	75.0	1.4692	99.0	2.5
2	Citronellal topes	45.0	1.4620	11.0	1.5
3	Citronellal	1005.0	1.4470	86.0	33.5
4	Citronellal lower	30.0	1.4675	19.5	1.0
5	Beta caryophyllene	45.0	1.4862	29.0	1.5
6	Citronellol topes	60.0	1.4625	21.0	2.0
7	Citronellol	120.0	1.4568	35.0	4.0
8	Geraniol topes	75.0	1.4730	43.0	2.5
9	Geraniol	900.0	1.4745	58.0	30.0
10	Geraniol lower	60.0	1.4735	55.0	2.0
11	Elemol	210.0	1.4615	45.0	7.0
Total recovery of the fractions		87.5%			
Percentage of residue		6.0%			
Loss of the material during processing			6.5%		

Table-6: Yield of various isolates in method-II

Sr. No.	Name of fractions	Wt. of fraction (gm)	Refractive index n20/D	Purity by GLC (%)	Yield of fractions (%)
1	Limonene	75.0	1.4690	89.0	2.5
2	Citronellal topes	45.0	1.4520	21.0	2.0
3	Citronellal	1005.0	1.4485	89.5	33.5
4	Citronellal lower	45.0	1.4635	19.5	1.5
5	Beta caryophyllene	30.0	1.4895	38.0	1.0
6	Citronellol topes	120.0	1.4625	23.7	4.0
7	Citronellol	150.0	1.4537	54.5	5.0
8	Geraniol topes	165.0	1.4735	28.0	5.5
9	Geraniol	915.0	1.4740	60.0	30.5
10	Geraniol lower	150.0	1.4745	38.0	5.0
Total recovery of the fractions		90.5%			
Percentage of residue		5.0%			
Loss of the material during processing			4.5%		

Table-7:
Product cost : It is based on the average yield

Products	Yield (%)	Quantity (kg)	Current market rate (Rs.)	Total value (Rs)
Citronellal	34.0	63.0	750.00	47250.00
Terpene/tops	3.0	5.5	200.00	1080.00
Beta caryophyllene	1.5	2.8	350.0	980.0
Geraniol tops	2.0	3.5	350.0	1225.0
Citronello/tops	1.0	1.8	350.00	630.00
Elemol	6.0	15.0	400	6000.00
Total Cost of Products = Rs. 114890.00				
Average Loss in process-5.5%				

Table-8 Products cost

Products	Yield (%)	Quantity (kg)	Current market rate (Rs.)	Total value (Rs)
Citronellal	90.0	57.0	950.00	54150.00
Topes	2	1.25	200.00	250.00
Intermediate tops	2	1.25	350.00	440.00
Residue	3	2.0	350.00	700.00
Total Cost of Products = Rs. 55540.00				
Average Loss in process-3%				

Table-9 Profit margin

Products	Raw Material cost including processing charges (Rs)	Products cost (Rs)	Net profit (Rs.)	Profit per Kg (Rs.)
Citronellal, Geraniol, beta Caryophyllene, Elemol, Limonene and others	104400.00	114890.00	10490.00	58.00
Citronello	53550.00	55540.00	1990.00	31.50

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