# Deterpenation of Orange Essential Oil by Molecular Distillation

Miriam A.Martinello[#1], Cecilia L. Pagliero[#2], Carolina A. Allevi.[#3]

*Facultad de Ingeniería, Universidad Nacional de Río Cuarto,*
*Ruta 36 Km 603, X5800BYA Río Cuarto, Argentina*
*Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICET) Argentina*

*Abstract* — *the influence of two operative conditions in the orange essential oil deterpenation by molecular distillation: rotor speed (100-200 rpm) and evaporation temperature (19-33ºC), on oxygenated compounds (linalool) recovery (LR) and on the oxygenated compounds monoterpenes concentration ratio (CR) were studied. A central composite design and the response surface methodology were employed for experimental design and for the molecular distillation process modelling, respectively.*

*It was found that the maximum concentration ratio is obtained at the lowest rotor speed and at an inter-mediate temperature level while the linalool recovery decreases with temperature and rotor speed. So, the best conditions to achieve a high concentration ratio (CR=10) and an acceptable linalool recovery (LR=65%) are 25ºC for evaporation temperature and 100 rpm for rotor speed. Higher concentration ratios could be obtained only if oxygenated compounds recovery is resigned.*

*Keywords* — *Molecular distillation, orange essential oil, response surface methodology, deterpenation.*

## I. INTRODUCTION

Citrus essential oils are used in the perfumery and food industry as flavoring agents. They contain a prevalent proportion of terpenic hydrocarbons (60-98%): mono-terpenenes, C10 H16, and sesquiterpenes, C15H24, and oxygenated terpenes (2-38%) as well as waxes, cumarin and psoralens. The major compound of orange essential oil is the monoterpene d-limonene and the major sesquiterpene is valencene.

The terpenic hydrocarbons take part more slightly than the oxygenated compounds in the aromatic profile of the essential oil. Not very odorous and partially unsaturated, they are chemically unstable and prone to structural regrouping in the presence of air, light and water, these reactions being accelerated by heat and low pH. All these modified compounds are undesirable because they can impart an off flavor when used to aromatize other products. The terpenic hydrocarbons are also in-soluble in water, which is a major disadvantage in the case of aromatization of drinks, which must remain limpid. They are also insoluble in polar solvents like alcohol which is a disadvantage in perfumery [1, 2].

Therefore, it is common industrial practice to remove some of the terpenes and as a consequence, to concentrate the oxygenated compounds which are mainly responsible for the characteristic citrus flavor and fragrance. This procedure is known as deterpenation or folding, and is currently done by vacuum distillation. There are references about other processes employed for this purpose, such as dilute alcohol extraction [3, 4] and vacuum distillation combined with liquid extraction [5,6]. These conventional techniques present several drawbacks, such as the formation of thermally degraded undesirable products, low yields and the presence of solvent residues.

Therefore other processes for orange oil deterpenation have been studied: supercritical fluid extraction with carbon dioxide [7, 8, 9], chromatographic adsorption [10], thin film evaporation [11, 12] distillation combined with microwaves [13].

Molecular distillation or short path distillation is a gentle method appropriate for the separation and purification of thermally unstable materials as well as compounds with a low vapour pressure and high molecular weight, without the hazard of thermal decomposition. This method is characterized by a short exposure of the distilled liquid to elevated temperatures, high vacuum in the distillation space, and a small distance between the evaporator and the condenser. So, molecular distillation has the advantage of avoiding compounds degradation due to the low pressures and low residence times, which characterize this operation [14, 15].

It is important to study the influence of operative conditions and equipment design in a process performance, in order to optimise it. For example Kumar and Jhinge [16] studied the influence of baffles orientation in a heat exchanger; Kannan and Kalathoor analysed the influence of particle size in a fluidised bed [17]. Concerning the operation applied in this work, the molecular distillation technique, there are several works available in the literature about the separation of mixtures of low volatility, thermal unstable materials such as octacosanol recovery from rice oil [18], extraction of bioactive compounds from oil deodorizer distillate [19, 20, 21], concentration of monoglycerides [22], vegetable oil

refining [23, 24], cocoa butter deacidification [25] and fish oil purification [26]. However, there are no many references about its application in essential oil concentration. Zeboudj et al. [27] and Tovar et al. [28] evaluated the optimum conditions for concentration by molecular distillation sweet orange oil and lemongrass essential oil, respectively.

The objective of this work is to analyse the influence of evaporation temperature and rotor speed in the product mass and concentration, related to those of the starting material, for the deterpenation of orange essential oil by molecular distillation.

## II. MATERIALS AND METHODS

The orange essential oils employed as the starting material for the experiments was provided by Argentinean citrus manufacturing company factory. Molecular distillation was performed in a KDL4 molecular distillation equipment, manufactured by UIC GmbH (Germany) available at the Engineering Faculty of the National University of Rio Cuarto (Argentina) (Fig. 1). It is equipped with a falling film evaporator (area: 0.04 $m^2$) and an internal condenser (area: 0.02 $m^2$). For feeding there is a jacketed vessel provided with a flow regulation valve and level indicator. The distillate and residue are collected in glass flasks. The vacuum system is composed of a mechanical pump and a diffusion pump. Condenser temperature (4.5ºC), operating pressure (10 Pa) and feed flow rate (4.2 $10^{-8}$ $m^3$/s) were the same in all the experiments. Feed temperature was set equal to evaporator temperature.



Fig. 1 KDL4 molecular distillation equipment (Eng. Fac.-UNRC).

The evaporator temperature and the wiping roller speed were changed in the range of 19- 33ºC and 100 -200 rpm, respectively.

For each one of the experiments two fractions were obtained: the distillate (enriched with monoterpenes) and the residue (enriched with oxygenated compounds). Two components were considered as key compounds: d-limonene for the light terpenic fraction and linalool for the oxygenated group.

In the starting orange oil the concentrations of these key compounds were: d-limonene= 95.17% and linalool= 0.38%. The composition of the, starting oil, the distillate and the residue fractions were determined by gas chromatography, employing a Hewlett Packard HP 5890 apparatus, provided with a capillary column Innowax and a FID detector. The gas carrier was nitrogen, with a flow of 2.5 10-8 m3 /s. The oven temperature followed a line-al program: 60ºC to 250ºC in 20 min, being maintained in the last value for 20 minutes. The injector and detector temperature were 250ºC and 350ºC, respectively.

Response surface methodology (RSM) was used for modelling the molecular distillation process. The experimental design employed for the analysis was a central composite design, which was modified due to the difficulty of setting the required values of rotor speed. The experiments consisted of 11 runs with two factors (evaporation temperature and rotor speed) and three replicates of the central point for the estimation of pure error (Table I).

Table I. Central composite design arrangement and responses

| Natural Variables | | Coded Variables | | Responses | |
|---|---|---|---|---|---|
| T (ºC) | RS (rpm) | $X_1$ | $X_2$ | LR | CR |
| 31 | 100 | 1 | -1 | 22.83 | 9.56 |
| 31 | 200 | 1 | 1 | 11.02 | 5.67 |
| 21 | 100 | -1 | -1 | 55,64 | 6.01 |
| 21 | 200 | -1 | 1 | 40.15 | 3.96 |
| 19 | 150 | -1.42 | 0 | 43.45 | 3.83 |
| 33 | 150 | 1.42 | 0 | 7.08 | 4.45 |
| 26 | 100 | 0 | -1 | 73.70 | 10.64 |
| 19 | 100 | -1.42 | -1 | 73.91 | 5.08 |
| 33 | 100 | 1.42 | -1 | 9.89 | 5.49 |
| 26 | 200 | 0 | 1 | 38.98 | 7.70 |
| 26 | 150 | 0 | 0 | 48.04 | 8.22 |
| 26 | 150 | 0 | 0 | 51.51 | 8.61 |
| 26 | 150 | 0 | 0 | 47.06 | 8.33 |

The response variables considered were linalool recovery in the residue fraction (LR) and the concentration ratio (CR), which were calculated as:

$$LR = \frac{R\,X_R}{F\,X_F} \qquad CR = \frac{X_R / Y_R}{X_F / Y_F}$$

Where R is the mass of residue and F is the mass of the feed. XR is the concentration of linalool and YR is the concentration of d-limonene in the residue, while XF and YF are the concentrations of the same compounds, but in the feed.

The relations between the coded and natural variables, for evaporation temperature and for rotor speed, are given bellow:

$$X_1 = \frac{T - T_c}{\Delta T} \qquad X_2 = \frac{RS - RS_c}{\Delta RS}$$

Where X1 and X2 are the coded values, T and RS are the corresponding natural values. Tc and RSc are the natural values in the center of the domain: Tc=26ºC, RSc=150 rpm. ΔT and ΔRS are the increments of T and RS corresponding to one unit of X1 and X2 respectively: ΔT=5ºC, ΔRS=50 rpm.

The software InfoStat [29] was used to analyse the experimental data.

The model proposed for each response is a second order model, whose coefficients were generated by regression analysis using the Marquart method.

The fitness of the model was evaluated by the correlation coefficient R2, the fraction of the variation explained by the model, and an analysis of variance (p-value) for the whole model and each one of the considered factors.

The effects of the variables were displayed in surface and contour plots.

## III. RESULTS AND DISCUSSION

The regression models obtained for linalool recovery (LR) and concentration ratio (CR) are given by :

$$LR = 49.350 - 15.637\ X_1 - 11,893\ X_2 \\ + 3.925 X_1\,X_2 \\ - 12.302\ X_1^2 + 0.794\ X_2^2$$

$$CR = 8.579 + 0.549\ X_1 - 1.422\ X_2 \\ - 0.027\,X_1\,X_2 \\ - 2,345\ X_1^2 + 0.182\ X_2^2$$

The correlation coefficients are high enough for a response surface: $R^2 = 91.2428$, $R^2$(adjusted)= 84.9877 for the LR model, and $R^2 = 91.3971$ ; $R^2$ (adjusted)= 85.2522 for the CR model.

The results of the analysis of variance for both models (Table II) indicate that there is a statistically significant multiple relationships between the independent variables and the response, for a confidence level of 99% (model p-value < 0.01).

Table II. Analysis of Variance

| Source of variation | Sum of squares | Degree of Freed. | Mean Square | F-Coef. | p-Value |
|---|---|---|---|---|---|
| **Linalool Recovery model** | | | | | |
| Model | 5396.36 | 5 | 1079.2 | 14.6 | 0.001 |
| Residue | 517.926 | 7 | 73.989 | | |
| Total | 5914.29 | 12 | | | |
| **Concentration Ratio Model** | | | | | |
| Model | 54.6099 | 5 | 10.922 | 14.8 | 0.001 |
| Residue | 5.14024 | 7 | 0.7343 | | |
| Total | 59.7501 | 12 | | | |

All the effects presented statistical influence, for a level of confidence of 95%, on the dependent variables LR and CR, excepting the interaction factor ($X_1 X_2$) and the rotor speed quadratic factor ($X_2^2$): it can be observed in Table III their p-value are greater than 0.05 (which means they are not statistically significative for a level of confidence of 95%).

So, both models could be simplified eliminating the interaction and quadratic rotor speed terms.

Table III. Main effects of temperature and rotor speed, the interaction between them and their quadratic terms.

| Parameter | Estimated value | Standard error | t-stat. | p-value |
|---|---|---|---|---|
| mean | 49.35 | 4.53 | 10.89 | 0.0000 |
| $X_1$ | -15.64 | 2.71 | -5.76 | 0.0007 |
| $X_2$ | -11.89 | 3.24 | -3.66 | 0.0080 |
| $X_1^2$ | -12.30 | 2.97 | -4.14 | 0.0043 |
| $X_2^2$ | 0.79 | 4.98 | 0.16 | 0.8779 |
| $X_1 X_2$ | 3.92 | 3.33 | 1.18 | 0.2766 |
| mean | 8.58 | 0.45 | 19.00 | 0.0000 |
| $X_1$ | 0.55 | 0.27 | 2.03 | 0.0819 |
| $X_2$ | -1.42 | 0.32 | -4.40 | 0.0031 |
| $X_1^2$ | -2.34 | 0.29 | -7.93 | 0.0001 |
| $X_2^2$ | 0.18 | 0.49 | 0.37 | 0.7243 |
| $X_1 X_2$ | -0.03 | 0.33 | -0.08 | 0.9363 |

The response surface for LR and CR are shown in Fig. 2 and Fig. 3, respectively.

The Durbin-Watson statistic, that examines the residues in order to determine if there is any significate correlation based in the order the data were introduced, is 1.25134 (p-value=0.0776) for the LR model and 1.94805 (p-value=0.4394) for the CR model. Since their p-value are greater than 0.05 it can be stated that there is no serial correlation in the residues.
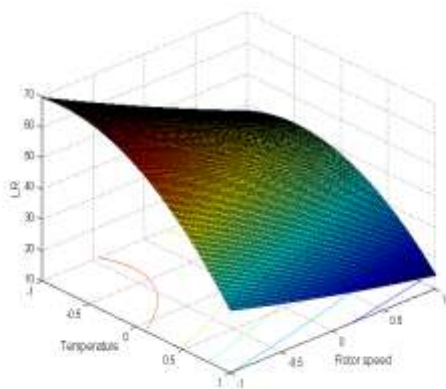


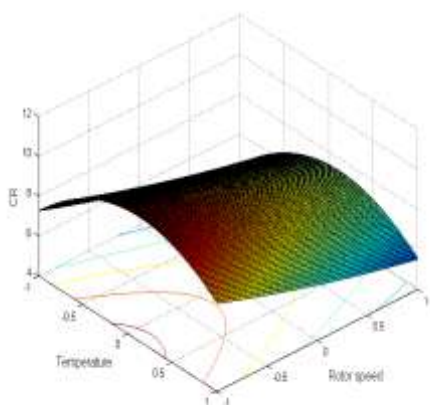Fig. 2 Response surface for the effect of temperature and rotor speed on Linalool Recovery



Fig. 3 Response surface for the effect of temperature and rotor speed on Concentration Ratio

Linalool recovery decreases as evaporator temperature and rotor speed increase. Rotor speed is related to residence time: higher rotor speed leads to higher residence time for the essential oil in the distillator. The effect of temperature and rotor speed are both relevant, being the temperature the one with more influence, in the experimental conditions studied. When the level of T is increased from -1 to +1, LR decreases 59 % (for RS level -1) and 72% (for RS level +1). When the level of RS is increased from -1 to +1, LR decreases 28 % (for T level -1) and 52% (for RS level +1). The coefficients in the model and the p-value for both effects lead to the same conclusions.

Since linalool is recovered in the residue fraction, as distillation conditions become more rigorous the quantity of this compound that goes to the distillate

fraction increases, that is along with the more volatiles monoterpenes, the oxygenates compounds are also evaporated.

Concentration ratio decreases as rotor speed increases and presents a maximum with temperature. The maximum is observed at an intermediate value of temperature (26.5 ºC) for all RS levels and its value decreases as RS level increases. So, for obtaining the highest CR value (about 10 in the range of experimental conditions studied) the minimum value of RS and a temperature of 26.5 ºC should be employed. In order to achieve a selective evaporation, so as to obtain a high relationship oxygenates/monoterpenes in the residue the residence time must be as low as possible and evaporation temperature should be kept in an intermediate value in order to limit the evaporation of oxygenates compounds along with the monoterpenes compounds.

Areas of optimum performance in the range of experimental conditions studied were located by superimposing contour plots for linalool recovery and concentration ratio (Fig. 4).
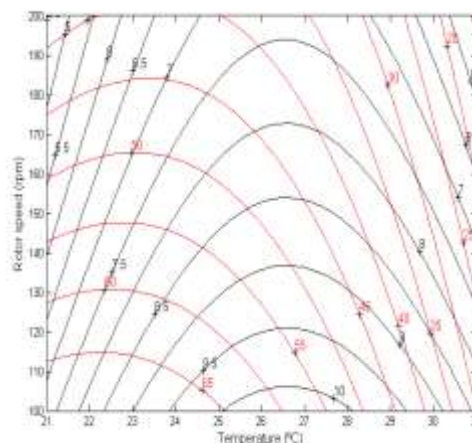


Fig. 4 Superimposed contour plot for linalool recovery and concentration ratio.

The maximum concentration ratio is obtained at the lowest rotor speed and at an intermediate temperature level while the linalool recovery decreases with temperature and rotor speed. So, the best conditions to achieve a high concentration ratio (CR=10) and an acceptable linalool recovery (LR=65%) are T=25ºC and RS=100 rpm. Higher concentration ratios could be obtained only if oxygenated compounds recovery is resigned.

### IV. CONCLUSIONS

Molecular distillation showed to be a proper method for orange oil deterpenation, allowing the concentration of oxygenated compounds in the residue fraction.

The evaporator temperature and the rotor speed are significant variables that affect the recovery of oxygenate compounds and the relationship between

oxygenates and terpenes concentration. Their most favorable values in the range of study were identified.

## REFERENCES

[1] F. Buccellato, "Citrus Oils in Perfumery and Cosmetic Products". *Perfumer & Flavorist*, vol. 25, pp. 59-63, 2000.

[2] R. Wildman, *Handbook of Nutraceuticals and Functional Foods.* CRC Press, USA, 2001.

[3] R. Sanchez, J. Pino, L. Chang, E. Roncal, E. Rogert, "Desterpenación de aceite esencial de naranja por extracción con etanol diluido", *Alimentaria* 249, pp. 59-63, 1994.

[4] J. Owusu-Yaw, R.F. Matthews, P. F. West,"Alcohol Deterpenation of Orange Oil", *J. Food Sci.*, vol. 51, pp.1180-1182, 1986.

[5] E. Haypek, E., L.H.M Silva, E. Batista, D.S. Marques, M. A. A., Meirelles, A.J. Meirelles, "Recovery of aroma compounds from orange essential oil", *Braz. J. Chem. Eng.* vol 17,pp. 4-7, 2000.

[6] G. Stuart, D. Lopes, V. Oliveira, "Deterpenation of Brazilian Orange Peel Oil by Vacuum Distillation", *J. Am. Oil Chem. Soc.* , vol 78, pp.1041- 1044 , 2001.

[7] P. Dugo, L. Mondello, K.D. Bartle, A. A Clifford, D. G, Breen, G. Dugo, "Deterpenation of Sweet Orange and Lemon Essential Oils with Supercritical Carbon Dioxide using Silica Gel as an Adsorbent", *Flavour Fragrance J*., vol. 10, pp. 51-58, 1995.

[8] M. Budich, S. Heilig, T. Wesse, V. Leibküchler, G. Brunner, "Countercurrent deterpenation of citrus oils with supercritical CO2", *J. Supercrit. Fluids*, vol. 14, pp.105-114, 1999.

[9] S. Diaz, S. Espinosa, E.A. Brignole, "Citrus peel oil deterpenation with supercritical fluids: Optimal process and solvent cycle design", *J. Supercrit. Fluids*, vol. 35, pp. 49-61, 2005.

[10] O. J Ferrer, R. F. Matthews, "Terpene reduction in cold pressed orange oil by frontal analysis-displacement adsorption chromatography". *J. Food Sci.,* vol. 52, pp. 801-805, 1987.

[11] J. D Vora, R.F. Matthews, P.G. Crandall, R. Cook, "Preparation and chemical composition of orange oil concentrates", *J. Food Sci*, vol. 48, pp. 1197-1199, 1983.

[12] F. Tateo,"Production of concentrated orange oil using thin evaporator", *J. Essential Oil Res*., pp.**7**-13, 1990.

[13] M. A. Ferhat, B. Y. Meklati, J.Smadja, F. Chemat, "An improved microwave Clavenger apparatus for distillation of essential oils from orange peel", *J. Chromatogr., A,* vol. 1112, pp. 121-126, 2006.

[14] A.Weissberger, *Destillation under high vacuum in technique of organic chemistry. Part 1: Distillation*, Interscience Publishers, 1951.

[15] R. Perry, D. Green, J. Maloney, *Perry´s Chemical Engineers´ Handbook,* Sixth Ed., McGraw Hill, 1984.

[16] N. Kumar, P. K. Jhinge, "Effect of segmental baffles at different orientation on the performance of single pass shell and tube heat exchanger", *Int. Journal of Ing. Trends and Technology*, vol. 15, pp. 423-428, Sept. 2014.

[17] A. Kannan, S. Kelathoor, "Mechanical agitation of bed in a motor driven two-phase fluidized bed particle seeder,", Int. *Journal of Ing. Trends and Technology*, vol. 10, pp. 4383-4387, Oct. 2013.

[18] F. Chen, T. Cai, G. Zhao, X. Liao, L. Guo, X. Hu, "Optimizing conditions for the purification of crude octacosanol extract from rice bran wax by molecular distillation analysed using response surface methodology", *J. Food Eng*., vol. 70, pp. 47-53, 2005.

[19] P. F. Martin, V.M Ito, C.B.Batistella,M.R.W. Maciel, "Free fatty acid separation from vegetable oil deodoriser distillate using molecular distillation process", *Sep. Purif. Technol*., vol. 48, pp.78-84, 2006.

[20] L. R. Posada, J. Shi, Y. Kakuda, S. J. Xue, "Extraction of tocotrienols from palm fatty acids distillates using molecular distillation", *Sep. Purif. Technol*. vol. 57, pp. 220-229, 2007.

[21] P. Shao, S.T. Jiang, Y.J. Yiang, "Optimization of molecular distillation for recovery of tocopherol from rapeseed oil deodorizer distillate using response surface and artificial neural network models", *Trans IChemE, Part C* , vol. 85, pp. 85-92, 2007.

[22] L. V., Fregolente, P. B. L., Fregolente, A.M. Chicuta, C. B. Batistella, R. Maciel Filho, M R. Wolf Maciel, "Effect of operating conditions on the concentration of monoglycerides using molecular distillation", *Trans IChem, Part A* , vol. 85, pp. 1524-1528, 2007.

[23] J. Cvengros,"Physical Refining of Edible Oils". *J. Am. Oil Chem. Soc.*, vol. 72, pp. 1193-1196, 1995.

[24] M., Martinello, G. Hecker, , M. Pramparo, "Grape seed oil deacidification by molecular distillation: Analysis of operative variables influence using the response surface methodology", *J. Food Eng*., vol. 81, pp. 60-64, 2007.

[25] W. Wu, C. Wang, J. Zheng, "Optimization of deacidification of low-calorie cocoa butter by molecular distillation", *LWT-Food Sci. Technol*., vol. 46, pp. 563-570, 2012.

[26] Å. Oterhals, B. Kvamme, M. Berntssen, "Modeling of a short-path distillation process to remove persistent organic pollutants in fish oil based on process parameters and quantitative structure properties relationships", *Chemosphere*, vol. 80, pp. 83–92, 2010.

[27] S. Zeboudj, N. Belhaneche-Bensemra, R. Belabbes, "Use of surface response methodology for the optimization of the concentration of the sweet orange essential oil of Algeria by wiped film evaporator", *J. Food Eng*., vol. 67, pp. 507-512, 2005.

[28] L. P. Tovar, M. R. Wolf Maciel, G. M. Ferreira Pinto, R. Maciel Filho, D. Ramalho Gomes, "Factorial Design applied to concentrate bioactive component of *Cymbopogon citratus* essential oils using short path distillation", *Chem. Eng. Res.& Des*., vol. 88, pp. 239-244, 2010.

[29] J. A. Di Rienzo, F. Casanoves, M. G. Balzarini, L. Gonzalez, M. Tablada,C. W Robledo,. *Software InfoStat*., Universidad Nacional de Córdoba, Argentina, 2011.