Application of instantaneous auto-vaporization process for essential oil extraction: case of Indonesian Ylang-Ylang flowers

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Full text

Extraction of Indonesian Ylang-Ylang Oil by Instantaneous Controlled Pressure Drop (DIC) Process

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Abstract

The extraction of Indonesian ylang-ylang oil was carried out by new process: Instantaneous Controlled Pressure Drop (DIC). This process involves subjecting the dried ylang-ylang (*Cananga odorata* Hook. fil. et Thomson, *forma macrophylla*) flowers for a short period time to a saturated steam pressure, followed by an abrupt pressure drop into vacuum (about 50 mbar). This abrupt pressure drop provokes simultaneously auto-vaporization of the volatile compounds, instantaneous cooling, swelling and breaking of cellular walls. The effect of process parameters, namely number of DIC cycles (1-9), steam pressure (2 - 6 bar), and total processing time (0.5-20 min) on the essential oil yield and its composition was examined. The results indicated a significant increase of oil yield with increasing processing pressure and number of DIC cycles, however the processing time was not a significant parameter. The DIC has been compared with a conventional technique, steam distillation (SD). The DIC exhibited better results than SD in terms of rapidity (4 min versus 24 h), oil yield (2.74% versus 2.60%) and also oil quality.

Keywords: Ylang-Ylang (*Cananga odorata* Hook. fil. et Thomson, *forma macrophylla*), extraction, essential oil, steam distillation, Instantaneous Controlled Pressure Drop

1. Introduction

The ylang-ylang tree, *Cananga odorata* Hook. fil. et Thomson, is a native of tropical Asia. Its essential oil is one of the most important perfume raw materials [1]. This oil is also used extensively in soap and detergents; aromatherapy; pharmaceutical industry; cosmetics and food flavors [2-6].

Ylang oil is isolated by steam distillation and sometimes by solvent extraction from fresh mature flowers [2, 3]. Low yield, losses of volatile compounds, long extraction times, toxic solvent residues, and degradation of unsaturated compounds, giving undesirable off-flavour compounds, due to heat may be encountered using these extraction methods [2, 7-9, 10]. These shortcomings have led to the consideration of the use of supercritical fluids in essential oil extraction processes. CO_2 is the most commonly used supercritical fluid because of its modest critical conditions. Furthermore, the supercritical CO_2 extraction of aromatic plants gives high quality and solvent-free extracts [9-16]. However, its high cost related to specific equipments for high-pressure conditions (200 bar), requirement of CO_2 purity and CO_2 low dielectric constant (thus giving rise to a non-polar character that hinders or makes difficult the extraction of polar compounds) make important the searching for new extraction method [17, 18].

The need of more rational technique for obtaining high quality essential oils has led our laboratory to develop a new and alternative extraction process: Instantaneous Controlled

Pressure Drop (DIC) [19]. The DIC process is based on the thermo-mechanical effects induced by subjecting the raw material for a short period of time to a saturated steam pressure (about 1 to 6 bar according to the product), followed by an abrupt pressure drop towards vacuum (about 50 mbar). This abrupt pressure drop ($\Delta P/\Delta t > 5$ bar.s^{-1}) provokes simultaneously auto vaporization of volatile compounds, instantaneous cooling of the products allowing to stop thermal degradation, swelling and eventually implies the rupture of cell walls, which enhances the global mass transfer.

The main objective of this work was to determine the optimum parameters of DIC process on the ylang oil extraction, and compare the results with oil obtained by steam distillation. We intend to make appropriate comparison in term of oil yield and composition.

2. Experimental

For evaluating DIC performance on essential oil extraction, we have realized the quantitative and qualitative comparative study between Steam Distillation (SD) and DIC extraction of ***dried*** ylang flowers. In this work, we have studied 3 parameters of DIC process: (1) The processing steam pressure which varied from 2 bar to 6 bar; (2) The total processing time varying from 0.5 to 20 minutes and (3) The number of DIC cycles varying from 1 to 9.

2.1. Materials

Fully mature Ylang-Ylang flowers (*Cananga odorata* Hook. fil. et Thomson*, forma macrophylla*) were picked up at blossom in Lawang, East Java, Indonesia (October 2003). The flowers were air-dried to a final moisture content of 10.2 % dry basis and stored at room temperature prior to use

2.2. Extraction methods

2.2.1. DIC apparatus and procedure

The schematic diagram of the equipment used has been described in a previous study [20]. This equipment is composed of three main elements:

- The autoclave (6L) where the flowers were placed and treated
- The vacuum system which consists mainly of a vacuum tank (285 L) and a water ring vacuum pump
- A pneumatic valve (100 mm spherical valve), which separates the processing vessel from the vacuum tank and can be opened in less than 200 ms to assure instantaneous pressure drop.

40 g of dried ylang-ylang flowers was treated in the autoclave in which a vacuum of 50 mbar was established by a brief connection with the vacuum tank. The initial vacuum treatment (Fig. 1a) facilitates the diffusion of steam into flowers. Consequently, the time necessary for heating the flowers to the temperature of the steam is reduced. Saturated steam is then injected into the autoclave at a fixed pressure level (Fig. 1b) and maintained for a determined time. An abrupt pressure drop follows this step (Fig. 1c). The equilibrium pressure after pressure drop depends on the operating pressure in the autoclave: the higher the operating pressure, the higher the equilibrium pressure. The vapour in the Ylang-Ylang flowers created by auto-vaporization after instantaneous pressure drop produces mechanical stresses which can deform or even break cells. This effect depends on the rheological properties of the plants which are function of humidity and temperature. Auto-vaporization as an adiabatic transformation induces instantaneous cooling of the residual product from 120-160°C (depending on the steam pressure) to about 30-35°C. The final temperature is

proportional to the given final pressure. The next step is either the thermal treatment by steam followed by pressure drop or return to atmospheric pressure (Fig. 1d).

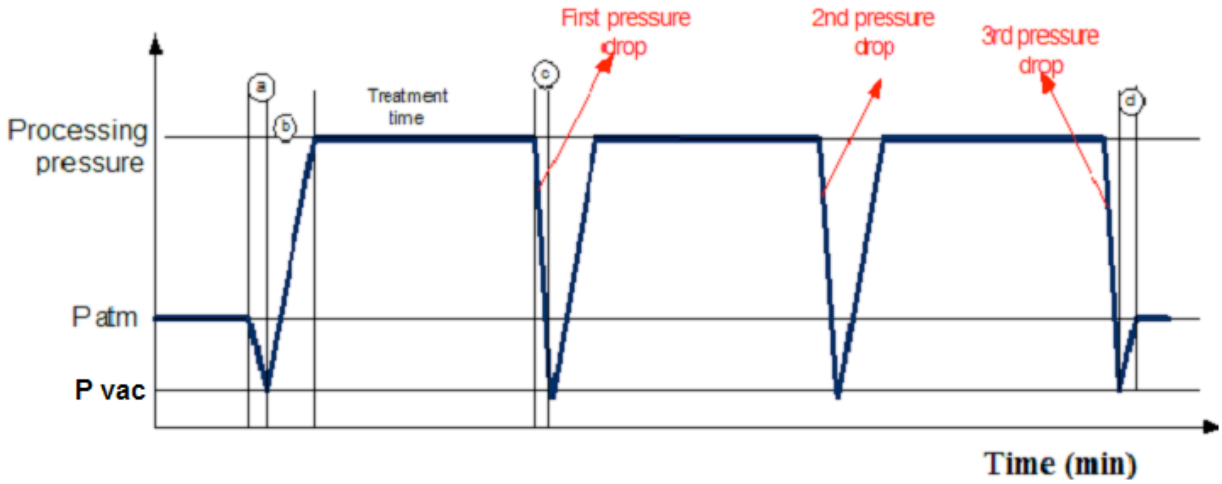


Figure 1. Several cycles of DIC treatment

If the DIC process is composed of several cycles, the treatment time is the total time during which a sample is exposed to the steam pressure.
The treatment time of 1 cycle of DIC is then defined as the ratio of the treatment time to the number of DIC cycles.

After DIC treatment, the condensate (oil-in-water emulsion) was recovered from an extract container connected to the vacuum tank. The vacuum tank is equipped with cooling water jacket. Then this emulsion was subjected to liquid-liquid extraction step in order to isolate essential oil.

2.2.2. Steam distillation of flowers

A packed bed of 80 g of dried ylang-ylang flowers was put on a stainless steel grill fixed above 2 L of water in the extraction vessel. The steam, which is produced in the lower part of the apparatus by electric heating, passes through the ylang bed evaporates and carries the essential oil. These vapours are condensed and the water is recycled into the extraction vessel.

2.2.3. Liquid-liquid extraction of the aqueous extracts

Prior to analysis, the critical stage was the oil separation from the condensate obtained after the steam distillation and DIC extraction. The condensate was extracted three times with chloroform with addition NaCl to facilitate the emulsion breakdown. Sodium sulphate was added to remove moisture and the organic phase was then dried under vacuum in a rotary-evaporator at 30°C. Each dried sample was diluted with chloroform to 20 ml and stored in the dark at 4°C prior to yield and composition analysis by GC-MS.

2.3. Analytical methods

2.3.1. Extraction yield

The yield of DIC oil and steam distilled oil was based on dry plant mass:

$$Oil\ \ yield\ \ (\%) = \frac{oil\ \ mass}{mass\ \ of\ \ dry\ \ flowers} \times 100\% \qquad (1)$$

where the oil mass was computed from the GC peak area of all volatiles molecules

2.3.2. Gas chromatography–mass spectrometry identification

The volatile molecules were analysed by gas chromatography coupled to mass spectrometry (GC–MS) A Varian computerized system comprising a 3900 gas chromatograph equipped by a fused-silica-capillary column with a non-polar stationary phase poly (dimethylsiloxane) CP-Sil 8 (30 m × 0.25 mm × 0.25 µm film thickness) was connected to a 2100T mass spectrometer. . The measurements were performed under the following conditions: carrier gas He; flow rate 1 $mL.min^{-1}$; split 1:100; injection volume 0.1 µL; injection temperature 250°C; oven temperature progress from 60 to 170°C at 2.5°$C.min^{-1}$, from 170 to 250°C at 10 $C.min^{-1}$ and holding at 250 C for 5 min; the ionisation mode was electronic impact at 70 eV. Mass spectra and reconstructed chromatograms were obtained by automatic scanning in the mass range m/z 30-400 a.m.u at 2.2 $scan.s^{-1}$. Identification of the components was achieved by a comparison of their mass spectral fragmentation patterns with those stored in the data bank (Varian NIST MS Database 1998 and Saturn libraries) and the literature [21; 22]. Quantitative analysis was performed by peak area measurement.

2.3.3. Scanning electron microscopy

Scanning electron micrographs of the untreated and DIC treated flowers were taken with a Jeol 5410 LV SEM with the aim to observe their structural changes.

3. Results and discussion

3.1. Essential oil yield

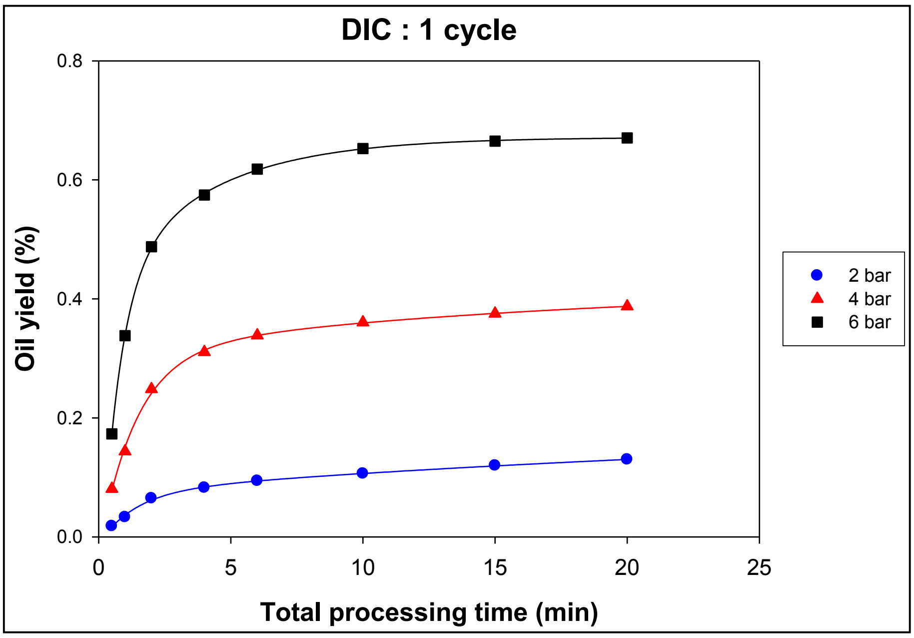
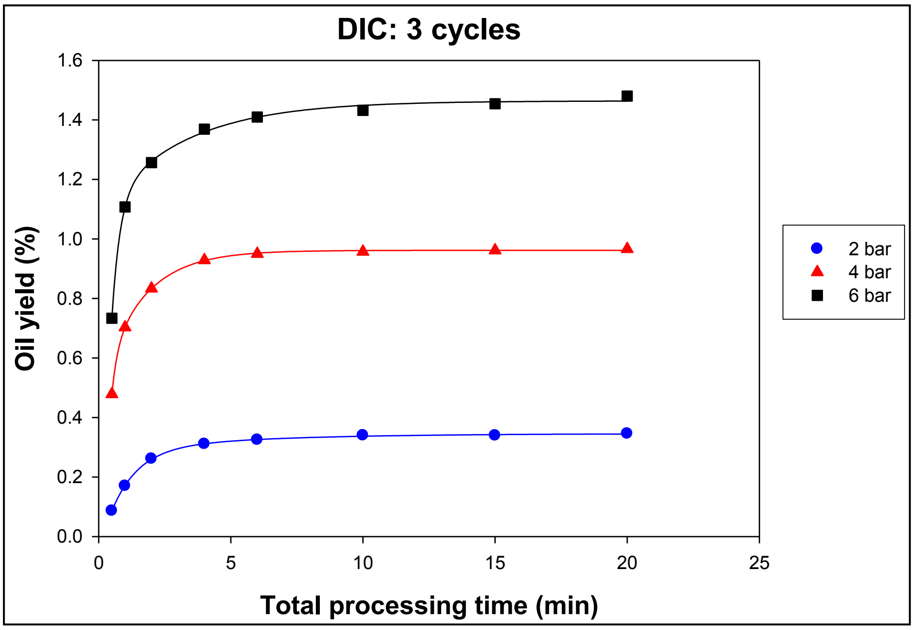
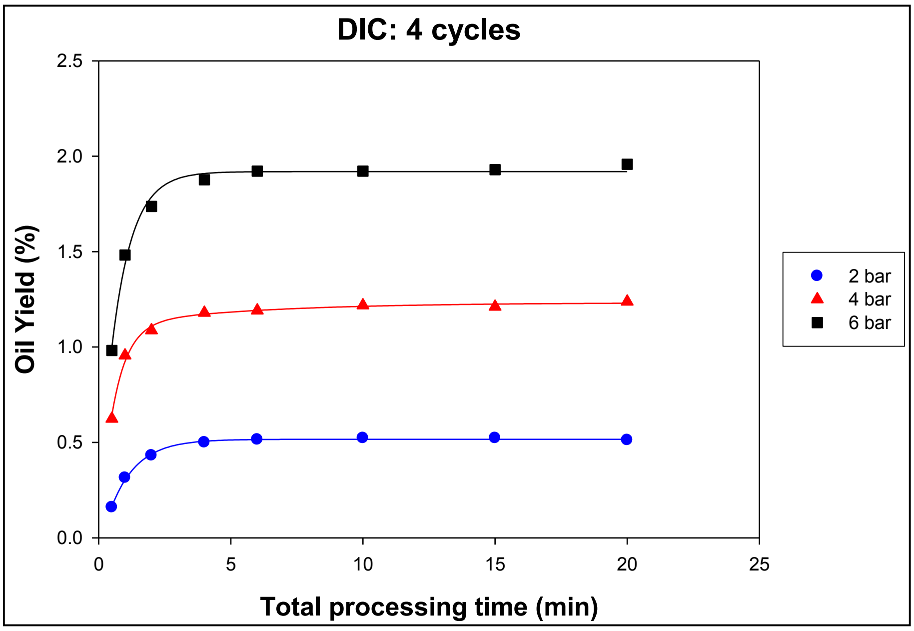


Figure 2. Effect of pressure and total processing time of DIC with 1 cycle on oil yield

The oil yield increases with increasing pressure and total processing time (see Fig. 2). The increase is considerable during the first 10 min. The processing pressure has a significant effect on the oil yield while the effect of total processing time after 10 min was not significant. When the pressure increases from 2 to 6 bar for a total time of 10 min, the oil yield increases from 0.11% to 0.65%. However, oil yield obtained by DIC with 1 cycle is very low (less than 1 %) in comparison to yield of industrial steam distilled oil from fresh flowers (about 2.0-2.5%) [23]. In order to increase oil yied, therefore the DIC extraction was carried out with several cycles and varying the processing time from 30 s to 20 min and pressure from 2 to 6 bar (see Fig. 3).



(a)



(b)

Figure 3. Effect of pressure and total processing time of DIC with several cycles on oil yield

The yield obtained by DIC with several cycles (see Fig. 3) has the same tendency as that of 1 cycle. The oil yield increases essentially with increasing pressure and total processing time during the first 6 min. A closer look at Figs. 2 and 3 shows that the increasing of number of cycles from 1 to 4 cycles at pressure 6 bar improve the oil yield three times; from 0.65% to 1.92%. Besides that, the increasing of processing pressure from 2 bar to 4 and 6 bar for 4 cycles improve the oil yield two times; from 0.52% to 1.20% and four times, from 0.52% to 1.92, respectively.

Interestingly, Figs. 2 and 3 also show that the more and more number of cycles, the shorter total processing time required for achievement of maximum yield (4 cycles in 6 min vs. 1 cycle in 10 min). After 4 cycles, the extended total processing time greater than 6 min results only a small gain in oil yield. Therefore, the total processing time was maintained at 6 min for further study of DIC cycle and processing pressure.

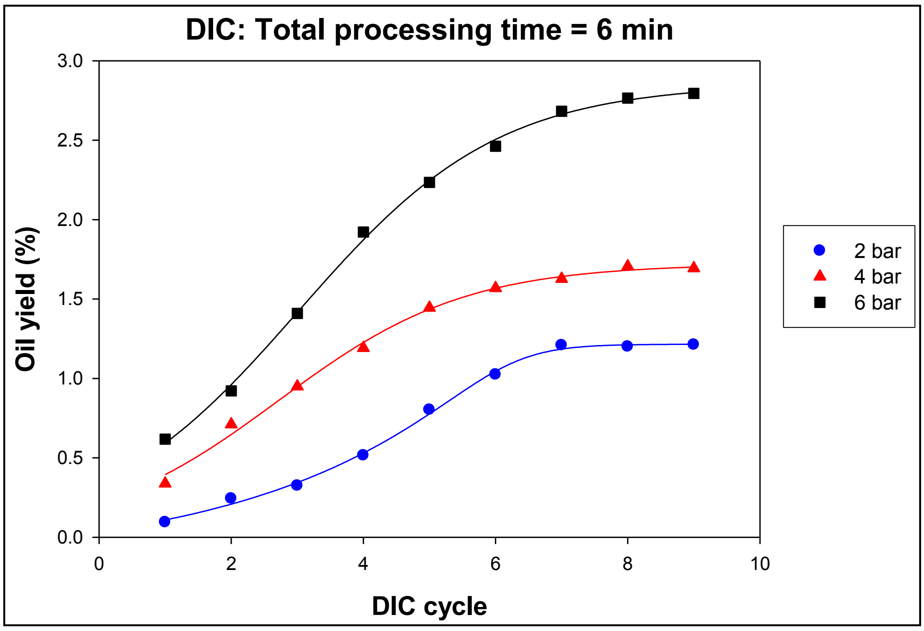


Figure 4. Effect of DIC cycle and processing pressure on oil yield

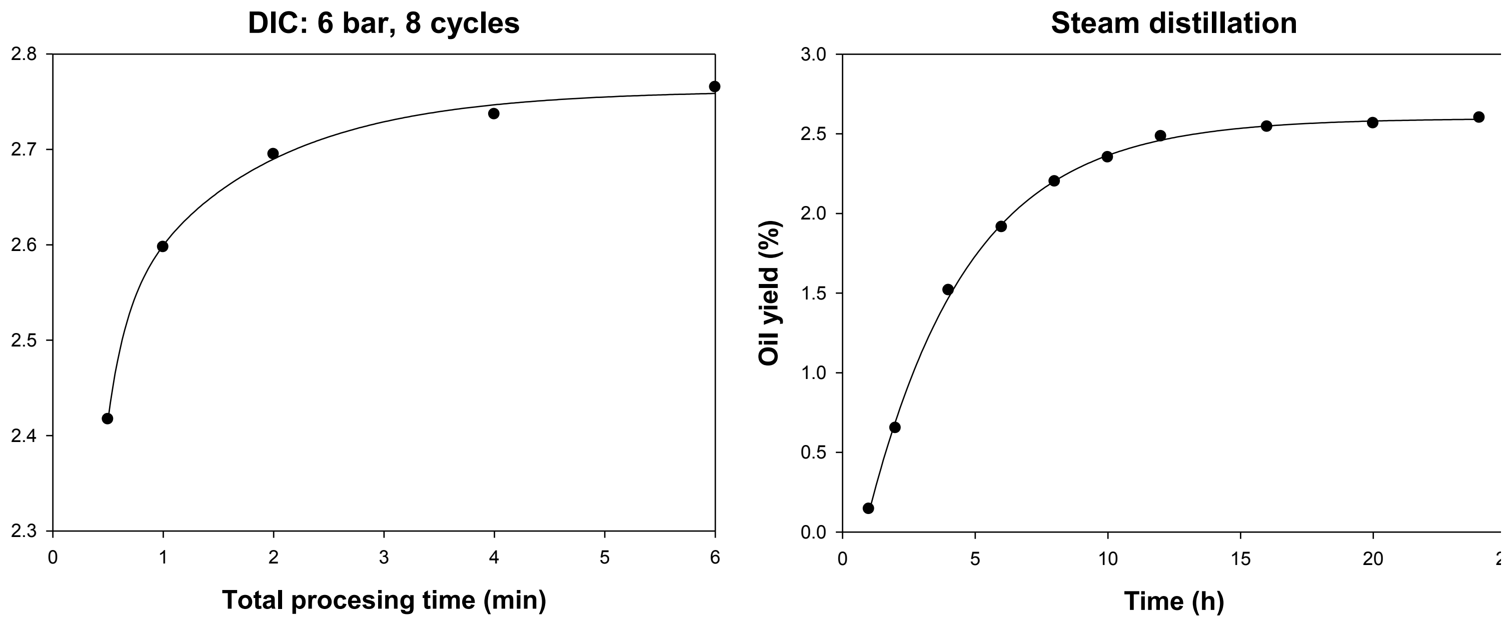
Oil yield as a function of the number of DIC cycles is shown in Fig. 4. The oil yield increases significantly with increasing processing pressure and DIC cycle. The oil yield achieved maximum after 8 cycles whatever the pressure used. It appears that the best result can be obtained at 6 bar with 8 cycles in 6 min with an oil yield of about 2.77%

An overall evaluation of the data from Figs. 2, 3 and 4 shows the most significant parameters of DIC process are the processing pressure and the number of cycles. The processing time is less significant. The effective time for each cycle is defined as the required time of heating steam for achievement of thermal equilibrium (the flowers temperature in the bulk is the same as that of steam) and rheological equilibrium (the achievement of flowers viscoelasticity required for swelling) [24]. It seems that a heating time of 45 seconds for each cycle (8 cycles in 6 min) is sufficient to reach the equilibrium conditions in case of ylang flowers.

These facts confirm that the extraction mechanism of DIC is based only on the instantaneous auto-vaporization of liquid complex (water + volatile oil) and modification of internal structure at each cycle. Therefore, the mass transfer is not controlled by internal diffusion, which characterizes the conventional extraction process. In addition, the compounds-solid matrix interaction that leads to importance of auto-vaporization of these compounds from the modified structures needs to be taken into account when considering the overall extraction kinetics. This is the explication for S-shaped of yield-cycle plot in Fig. 4 for DIC with pressure of 6 bar. We observed a slow rate of rise at first cycle and then speeding up before dropping to zero at the last cycle.

As the number of pressure drop (i.e. number of DIC cycle) increases, especially when high-pressure steam applied, the alveolation becomes more prominent (formation of wide, deep and interconnected-pores) and results in a higher breaking rate of cell walls. Such complex micro-alveolation structure allows auto-vaporization and liberation of imprisoned-compounds within endogenous site in the following pressure drop.
Beside of the processing parameters, the internal structure modification depends also on the nature of flowers (physical, thermal stability, moisture content, etc).

A great advantage of the DIC method is its rapidity. The results of a comparative study of extraction kinetics of the steam distillation and the DIC process (6 bar and 8 cycles) are shown in Fig. 5. In case of DIC process, the increase of oil yield is considerable during the first 4 minutes. In contrast, the steam distillation required 12 h for isolating of 95% of essential oil. The yield of the DIC with of 8 cycles during a total processing time of 4 min (2.74%) at 6 bar was comparable to that obtained after 24 h by means of steam distillation (2.60%), which is the reference method in essential oil extraction. These results confirm a substantial saving of time, energy and plant material by using the DIC process. In conclusion, the process parameters of 6 bar, 8 cycles and 4 or 6 min can be regarded as optimum for Indonesian ylang oil extraction.



(a) (b)

Figure 5. Comparison of kinetics extraction between DIC at 6 bar, 8 cycles (a) and steam distillation (b)

Beside of the quantity aspect, the performance of an extraction method is appreciated according to high quality of oil produced. For this purpose, a comparison of chemical composition of ylang oil obtained by DIC and steam distillation methods was made. The results are summarized in next chapter.

3.2. Composition of essential oil

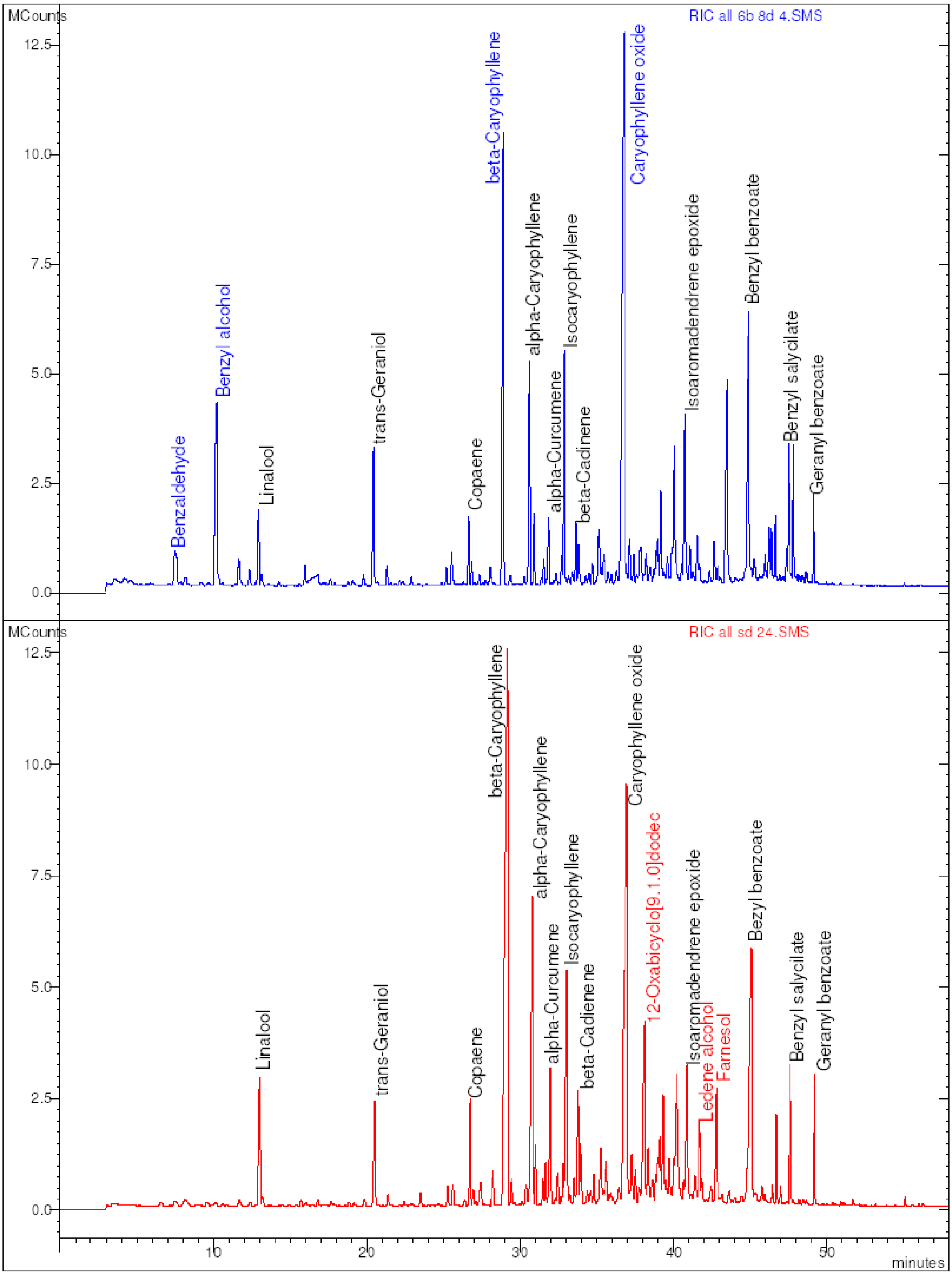


Figure 6. Comparison of gas chromatograms of Indonesian ylang-ylang oil obtained by DIC at 6 bar, 8 cycles, 4 min (above) and SD during 24 h (below).

Table 1. The chemical composition of Indonesian ylang-ylang oil obtained by SD and DIC

No	Retention time (min)	Compounds	Type	Steam distillation 24 h	DIC 6 bar, 8 cycles, 4 min
1	**7.682**	**Benzaldehyde**	**LOC**	**0.13%**	**1.21%**
2	8.151	5-Hepten-2-one	LOC	0.24%	0.24%
3	**10.13**	**Benzyl Alcohol**	**LOC**	**0.08%**	**5.51%**
4	11.652	cis-Linalool Oxide	LOC	0.12%	0.58%
5	12.385	trans-Linalool Oxide	LOC	0.06%	0.28%
6	**13.029**	**Linalool**	**LOC**	**2.26%**	**1.40%**
7	13.186	3-Octyne-2-one	LOC	0.15%	0.20%
8	16.038	Benzyl acetate	LOC	0.08%	0.30%
9	19.855	beta-Citral	LOC	0.00%	0.13%
10	**20.53**	**trans-Geraniol**	**LOC**	**1.56%**	**2.40%**
11	21.391	Geranial	LOC	0.13%	0.28%
12	25.281	alpha.-Cubebene	S	0.23%	0.24%
13	25.64	Eugenol	LOC	0.26%	0.55%
14	**26.763**	**Copaene**	**S**	**1.32%**	**1.01%**
15	26.969	Geranyl acetate	LOC	0.23%	0.31%
16	28.255	Methyl eugenol	LOC	0.53%	0.38%
17	27.356	beta-Cubebene	S	0.21%	0.17%
18	27.463	(-)-beta-Elemene	S	0.33%	0.00%
19	**29.218**	**beta-Caryophyllene**	**S**	**18.20%**	**9.85%**
20	29.468	Bicyclo[4.4.0]dec-1-ene	S	0.38%	0.18%
21	30.394	n.i.	S	0.35%	0.14%
22	**30.852**	**alpha.-Caryophyllene**	**S**	**6.52%**	**3.82%**
23	31.035	alpha-Curcumene	S	0.71%	0.92%
24	31.509	Epizonarene	S	0.30%	0.10%
25	31.675	gamma-Muurolene	S	0.53%	0.37%
26	**31.961**	**1H-Cyclopenta[1,3cyclopropa[1,2]**	**S**	**2.05%**	**1.15%**
27	32.466	(+)-Epi-bicyclosesquiphellandrene	S	0.42%	0.21%
28	32.834	alpha-Muurolene	S	0.59%	0.45%
29	**33.068**	**Isocaryophillene**	**S**	**4.25%**	**3.80%**
30	33.08	alpha.-Farnesene	S	-	0.03%
31	33.279	beta-Bisabolene	S	0.09%	0.10%
32	33.517	gamma-Cadinene	S	0.32%	0.15%
33	**33.804**	**beta-Cadinene**	**S**	**1.51%**	**1.00%**
34	33.948	Calamene + delta-Cadinene	S	0.91%	0.75%
35	34.41	Naphthalene,1,2,3,4,4a,7-hexahydro-	S	0.17%	0.11%
36	34.827	Cadala-1(10),3,8-triene	S	0.37%	0.30%
37	35.274	n.i.	HOC	1.07%	1.07%
38	35.629	Longipinocarveol trans	HOC	0.61%	0.64%
39	35.81	9-Methoxycalamenene	HOC	0.15%	0.19%
40	36.043	n.i.	HOC	0.09%	0.13%
41	36.477	3-Hexen-1-ol	HOC	0.37%	0.28%
42	**36.955**	**Caryophyllene oxide**	**HOC**	**13.75%**	**20.14%**
43	37.263	Aristolenene epoxide	HOC	0.82%	0.65%
44	37.546	n.i.	HOC	0.46%	0.40%
45	38.143	12-Oxabicyclo[9.1.0]dodeca-3,7-diene	HOC	4.01%	1.17%
46	38.367	Tricyclo[5.2.2.0(1,6)]undecan-3-ol	HOC	1.00%	0.62%
47	38.852	Cubenol	HOC	0.40%	0.29%
48	39.027	Aromadendrene oxide-(1)	HOC	0.91%	0.51%
49	39.15	Aromadendrene oxide-(2)	HOC	1.07%	0.83%
50	39.359	Tetracyclo[6.3.2.0(2,5).0(1,8)tridecan-	HOC	1.63%	1.64%

51	39.762	Ledene oxide-(II)	HOC	0.72%	0.54%
No	Retention time (min)	Compounds	Type	Steam distillation 24 h	DIC 6 bar, 8 cycles, 4 min
52	40.043	Cedrenol	HOC	0.77%	0.73%
53	**40.221**	n.i˙	**HOC**	**2.44%**	**2.51%**
54	40.324	Cycloisolongifolene,8-hydroxy-,endo-	HOC	0.73%	0.57%
55	**40.916**	**Isoaromadendrene epoxide**	**HOC**	**2.72%**	**3.37%**
56	41.706	Ledene alcohol	HOC	1.30%	0.88%
57	42.835	(E,E)-Farnesol	HOC	1.85%	0.73%
58	**43.564**	n.i.	**HOC**	**0.07%**	**4.97%**
59	**45.092**	**Benzyl benzoate**	**HOC**	**7.87%**	**6.52%**
60	45.945	n.i.	HOC	0.09%	0.24%
61	46.461	n.i.	HOC	0.16%	0.57%
62	46.73	n.i.	HOC	0.81%	0.60%
63	47.442	Platambin	HOC	0.02%	0.41%
64	**47.617**	**Benzyl salycilate**	**HOC**	**1.49%**	**1.63%**
65	**47.768**	**4,4,8-Trimethyltricyclo[6.3.1.0(1,5)]**	**HOC**	**0.02%**	**1.28%**
66	48.657	Oxacycloheptadecan-2-one	HOC	0.04%	0.10%
67	49.202	Geranyl benzoate	HOC	0.77%	0.61%

LOC: Light oxygenated compounds; S: Sesquiterpenes; HOC: Heavy Oxygenated Compounds
n.i. : non-identified

Table 2. Yield and grouped compounds of ylang oil obtained by SD and DC

Compounds	Percent in oil (%)	
	Steam distillation 24 h	DIC 6 bar, 8 cycles, 4 min
Light Oxygenated Compounds	5.84%	13.77%
Sesquiterpenes	39.75%	24.85%
Heavy Oxygenated Compounds	53.35%	60.15%
Oil yield (gr oil/100 gr DM)	2.60%	2.74%

The gas chromatograms of ylang-ylang oil obtained from dried flowers by DIC and SD techniques are shown in Fig. 6. The chemical composition of these oils is presented in Table 1. From 67 peaks 58 components were identified, which constitute more than 90% of the volatile fraction.

The components were grouped into compound families in order to better appreciate the effect of extraction method on the chemical composition of isolated oils (see Table 2). From Table 2, it can be seen that a substantially higher amount of oxygenated compounds and a lower amount of sesquiterpenes hydrocarbons are present in the ylang oil extracted by DIC in comparison with the steam distillation.

Value of ylang-ylang oils is determined by the content of oxygenated constituents and sesquiterpenes. The quality of ylang-ylang oil increases with the content of both light and heavy oxygenated compounds. The sesquiterpenic portion gives no more than a weak contribution to the typical ylang-ylang odour. As it is insoluble in alcohol, fine perfumery seeks the oils which are rich in oxygenated constituents. The sesquiterpenic oils are used in soap manufacture. According to Buccellato [25], the oxygenated compounds (alcohols, esters, ethers, phenols and aldehydes) provide the medicinal, floral, spicy/balsamic and fruity note to the odour profile, whereas the sesquiterpenes contribute to the woody character only in ylang odour. It appears that the DIC process provided better quality of ylang oil than the steam distillation.

A lower content of sesquiterpenes in the DIC oil is probably due to the diminution of thermal degradation. The steam distillation uses a large quantity of water at a high temperature for a long time. Water is a polar solvent, which accelerates many reactions, especially via carbocation as intermediates. This results in hydrolytic, trans-esterification or oxidation reactions of the other compounds into sesquiterpenes.

The HOC and sesquiterpenes are the main components in the Indonesian ylang oil but their relative amounts differ according the extraction methods (see Table 1 and 2).

3.3. Scanning electron microscopy

To prove the mechanical effect of DIC treatment, the scanning electron microscopy of untreated and DIC treated flowers was realized

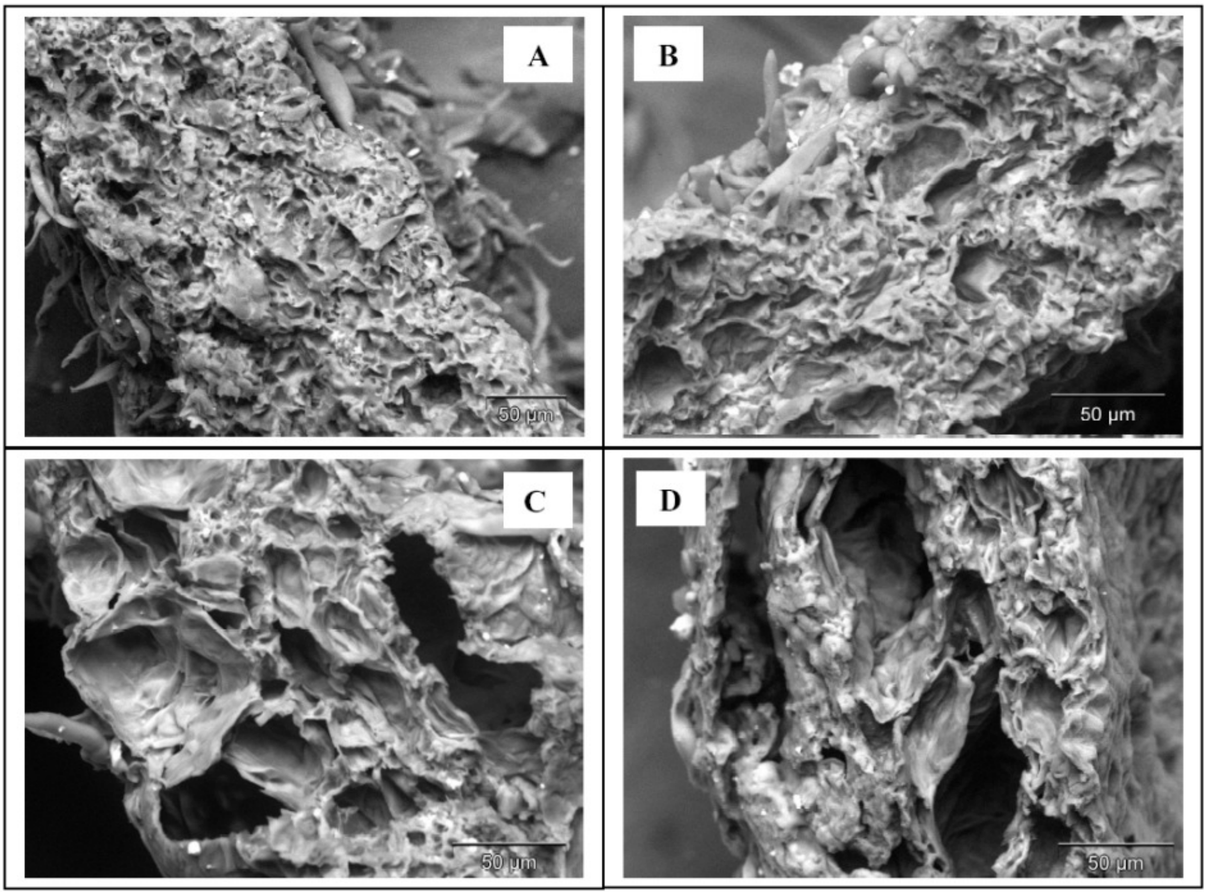


Figure 7. Scanning electron micrographs of untreated flowers (A) and DIC treated flowers at 2 bar, 1 cycle, 10 min. (B), 6 bar, 5 cycles, 4.4 min. (C), and 6 bar, 9 cycles, 10 min. (D).

Micrographs of the cross sections of untreated and DIC treated flowers are shown in Fig. 14. The structure of untreated flowers has alveoli of several µm (see Fig.17 A). The DIC treated flowers have a structure with larger alveoli with dimensions depending on the treatment conditions (see Figs. 17 B-D). These micrographs proved the aptitude of DIC on the modification of internal structure. The higher the processing pressure and the more the DIC cycles, the higher the degree of alveolation which results in a higher breaking rate of cells walls. This facilitates liberation and vaporization of volatile molecules.

4. Conclusions

The essential oil extraction from ylang flowers is very efficient by using the DIC process. The maximum oil yield (2.77%) is obtained with eight cycles at a steam pressure of 6 bar absolute and total heating time between 4 and 6 min. In comparison with the steam distillation, the DIC oil contains higher content of light and heavy oxygenated components (73.92% vs. 59.19%). In contrast, its sesquiterpenes content is lower (13.29% vs. 39.75%). The DIC treatment increases the availability of the heavy oxygenated components in the flowers. The structure of the flowers is more alveolated at the higher pressure and number of DIC cycle. The DIC can be also used as a pretreatment technique for the improvement of the solvent extraction or others conventional extraction techniques of non-volatiles compounds.

References

[1] E.E. Stashenko, W. Torres, J.R. Martinez Morales, A study of the compositional variation of the essential oil of ylang-ylang (*Cananga odorata* Hook fil. et Thomson, *forma genuina*) during flower development, Journal of High Resolution Chromatography. 18 (1995) 101-104.

[2] F. Buccellato, Ylang survey, Perfumer & Flavorist. 7 (1982) 9-13.

[3] E.M. Gaydou, R. Randriamiharisoa, J-P Bianchini, Composition of the essential oil of ylang-ylang (*Cananga odorata* Hook. fil. et Thomson, *forma genuina*) from Madagascar, J. Agric. Food Chem. 34 (1986) 481-487.

[4] Colgate to offer aromatherapy under Palmolive, Focus on Surfactants. 2003 (2003) 7.

[5] S.E. Lee, Biochemical mechanisms conferring cross-resistance to fumigant toxicities of essential oils in a chlorpyrifos-methyl resistant strain of *Oryzaephilus surinamensis* L. (*Coleoptera: Silvanidae*), Journal of Stored Products Research. 38 (2002) 157-166.

[6] J. Valnet, Aromathérapie, 11ème ed., Maloine, Paris, 1990.

[7] L.M. Assis, J.S. Silva Pinto, F.M. Lancas, Comparison among different extraction methods (PFE, SFE, Sonication, Soxhlet) for the isolation of organic compounds from coal, Journal of Microcolumn Separations. 12 (2000) 292–301.

[8] S.J. Lehotay, Supercritical fluid extraction of pesticides in foods, Journal of Chromatography A. 785 (1997) 289–312.

[9] M. Oszagyan, B. Simandi, J. Sawinsky, A. Kery, E. Lemberkovics, J. Fekete, Supercritical fluid extraction of volatile compounds from lavandin and thyme, Flavour Fragrance Journal. 11 (1996) 157–165.

[10] M. Sato, M. Goto, T. Hirose, Fractional extraction with supercritical carbon dioxide for the removal of terpenes from Citrus oil, Industrial & Engineering Chemistry Research. 34 (1995) 3941–3946.

[11] G. Anitescu, C. Doneanu and V. Radulescu, Isolation of coriander oil: comparison between steam distillation and supercritical CO_2 extraction. Flavour Fragrance Journal 12 (1997), pp. 173–176.

[12] E. Reverchon, Supercritical fluid extraction and fractionation of essential oils and related products. Journal of Supercritical Fluids 10 (1997), pp. 1–37.

[13] M. Goto, M. Sato, T. Hiroshe, Extraction of peppermint oil by supercritical carbon dioxide, Journal of Chemical Engineering of Japan. 26 (1993) 401–407.

[14] E. Reverchon, F. Senatore, Isolation of rosemary oil: comparison between hydrodistillation and supercritical CO_2 extraction, Flavour and Fragnance Journal. 7 (1992) 227–230.

[15] E. Reverchon, O. Sesti, D. Gorgoglione, Supercritical CO_2 extraction of basil oil: characterization of products and process modelling, Journal of Supercritical Fluids. 7 (1994) 185–190.

[16] F. Gaspar, T. Lu, R. Santos, B. Al-Duri, Modelling the extraction of essential oils with compressed carbon dioxide, Journal of Supercritical Fluids. 25 (2003) 247–260.

[17] F. Gaspar, R. Santos, M.B. King, Disruption of glandular trichomes with compressed CO_2: alternative matrix pre-treatment for CO_2 extraction of essential oils, Journal of Supercritical Fluids. 21 (2001) 11-22.

[18] M.D. Luque de Castro, M.M. Jiménez-Carmona, V. Fernández-Pérez, Towards more rational techniques for the isolation of valuable essential oils from plants, TrAC Trends in Analytical Chemistry. 18 (1999) 708-716.

[19] K. Allaf, S.A. Rezzoug, F. Cioffi, M.P. Contento, Processus de traitement thermo-mécanique par détente instantanée contrôlée des fruits, jus et peaux d'agrumes. French patent no. 98/11105, 1998.

[20] S.A. Rezzoug, M.W. Baghdadi, N. Louka, C. Boutekedjiret C., K. Allaf, Study of a new extraction process: Controlled instantaneous decompression. Application to the extraction of essential oil from rosemary leaves, Flavour Fragr. J. 13 (1998) 251-258.

[21] R.P. Adams, Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy, Allured Publishing Corporation, Carol Stream, 1995.

[22] S. Arctander, Perfume and Flavor Chemicals, Allured Publishing Corporation. Carol Stream, 1994.

[23] E. Guenther, The essential oils, Vol. 5, Van Nostrand, N.Y., 1952, pp. 276-316, 381.

[24] N. Louka, K. Allaf, Expansion ratio and color improvement of dried vegetables texturized by a new process "Controlled Sudden Decompression to the vacuum". Application to potatoes, carrots and onions, Journal of Food Engineering. 65 (2004) 233-243.

[25] F. Buccellato, Ylang survey, Perfumer & Flavorist. 7 (1982) 9-13.