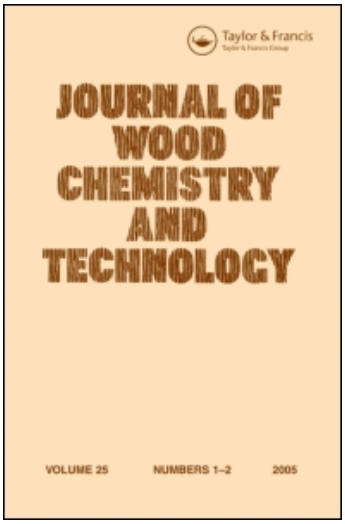

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Optimization of Steam Extraction of Oil from Maritime Pine Needles

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Abstract: Essential oil from pine maritime needles is generally extracted by steam distillation process at atmospheric pressure for more than one hour, or by solvent extraction process. In the last decade, there has been an increasing demand for new extraction techniques enabling automation, shorter extraction time, and reduced consumption of organic solvent. In this study, Response Surface Methodology (RSM) was used to evaluate the effects of two processing parameters of an alternative extraction process: instantaneous controlled pressure drop: "Détente Instantanée Contrôlée" (D.I.C.) on the yield and composition of oil isolated from maritime pine needles (*Pinus pinaster*). This process involves subjecting the substrate for a short time to steam varying from 1.5 to 5.5 bar (113 to 155°C) for 4 to 20 minutes, followed by an instantaneous decompression to a vacuum (about 50 mbar). We studied the effect of processing pressure and processing time on the yield of oil and in three important compounds: α-pinene, β-pinene, and germacrene D. Both the processing pressure and time had a significant effect on all responses studied. For the less volatile compound, α-pinene, the maximum quantity was obtained at the lower processing pressure and time, while an inverse trend was observed for β-pinene and germacrene D. The models displayed by the experimental design gave R^2 higher than 0.92.

Keywords: Isolation, maritime pine (*Pinus pinaster*), oil, thermomechanical process, vacuum

INTRODUCTION

Essential oil is any class of volatile oil of complex hydrocarbons, mainly terpenes and some other chemicals that are isolated from plants. One of their

Biolandes Society, located in Le Sen, Landes, France, is gratefully acknowledged for providing the maritime pine needles.

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characteristics is the generation of flavor or aroma. Essential oils extracted from plants such as pines are used as fragrances in cosmetics, flavoring additives of foods and beverages, and scenting agents in a variety of household products including detergents, soaps, or insect repellent. They are also used as intermediate in the synthesis of perfume chemicals and for unconventional medicinal purposes as well as in aromatherapy.[1,2] The conventional methods for extracting essential oils have some disadvantages. For steam distillation and hydrodistillation, elevated temperatures can cause chemical modifications of oil components and a loss of the most volatile compounds.[3] When using solvent extraction, it is impossible to obtain a solvent-free products and this process usually also results in the loss of volatile components. In contrast, extraction by supercritical fluids leads to high-quality and solvent-free extracts.[4] However, according to Temelli et al.[5] and Oszagyan et al.,[6] supercritical fluid extraction is costly. Moreover, several studies[7] have shown that CO_2 not only extracts essential oil, but also other compounds such as waxes or resins.

The Instantaneous Controlled Pressure Drop process, known as "D.I.C.," was developed and patented in our laboratory some years ago.[8,9] This process subjects the product to rapid transition from high steam pressure to vacuum. This transition induces a fast evaporation of water and volatile compounds. In a previous work,[10] we showed that processing by instantaneous controlled pressure drop increases the global diffusivity of the product and improves the availability of the liquid in the plant.

The essential oil isolation based on this process is an interesting alternative to standard techniques of essential oil extraction, such as extraction with solvents or steam distillation. This is because it does not use solvent, and induced cooling when the plant is rapidly transferred from a high steam pressure to vacuum minimizes thermal degradation of the essential oil components. Moreover, compared to the steam distillation, the short time contact (few minutes) between plant and the heated zones of apparatus avoids the loss and degradation of volatile and thermolabile compounds.

The objectives of this study were to evaluate the effect of two independents process variables, processing water steam pressure and processing time on: (i) the yield of oil isolated from maritime pine needles and (ii) the composition of the isolated oil in three commercially important compounds—α-pinene, β-pinene, and germacrene D. In addition, a mathematical model[11–13] predicting the yield allowed the optimization of the extraction process.

MATERIALS AND METHODS

Plant Material

Maritime pine (*Pinus pinaster*) was collected from plants growing in west southern France. The needles were used at their residual moisture content

Table 1. Coded levels for independent variables used in developing experimental data

		Coded level				
		$-\alpha$	−1	0	1	$+\alpha$
Processing pressure (bar)	P	0.67	1.5	3.5	5.5	6.32
Processing time (min)	t	0.68	4	12	20	23.31

α axial distance $= \sqrt[4]{N}$, N is the number of experiments of orthogonal design (i.e., of the factorial design). In this case $\alpha = 1.414$.

(63.1% dry wt basis). The compounds identified by steam distillation (see the section Steam Distillation) and their yields are shown in Table 1. The yield of essential oil in fresh raw material was 0.82% by mass (g of isolated oil/100 g dm). This value is in agreement with the values cited by Kelkar et al.,[14] and Dob et al.[15]

Experimental Set-Up

The experimental set-up was largely described in a recent paper.[16] It is composed of three main elements:

- The processing vessel where samples were placed and treated.
- The vacuum system, which consists mainly from vacuum tank with volume (360 l) 130 fold greater than the processing vessel (12 l), and a vacuum pump. The initial vacuum pressure of vacuum container was maintained at 50 mbar in all experiments.
- A pneumatic valve that separates the processing vessel from vacuum tank. It can be opened in less than 0.2 seconds; this ensures a rapid decompression within the reactor.

Protocol of Extraction by the Instantaneous Controlled Pressure Drop Process

The needles are placed in the D.I.C. vessel, which is maintained under vacuum (∼50 mbar) through its connection to a vacuum container. The vacuum allows a better diffusion of heating fluid through plant and consequently heat transfer between steam and wood is improved and time to reach the desired processing pressure (or processing temperature) is shortened. After closing the electropneumatic valve, which connects the reactor to the vacuum tank, an atmosphere of steam pressure (between 1 and 6 bar in this study) is created within the D.I.C.

reactor. After a processing time at fixed processing pressure, the thermal treatment is followed by a rapid decompression resulting in a rapid drop in pressure. The equilibrium pressure after decompression depends on operating pressure: the higher the processing pressure, the higher the equilibrium pressure. Evaporation, which is effected in adiabatic conditions, induces a rapid cooling of the residual product and the final temperature must be commensurate with final pressure. Extract and condensed steam are recovered in a specific container. The volume of obtained mixture was about 400 ml for all experiments.

Steam Distillation

Fifty g of maritime pine needles chips were placed on a stainless steel grid. This grid was placed in a glass chamber containing boiling water. The steam crossed the grid during 2 hours and was recovered along with volatiles after crossing a refrigerant. The condensates were separated into aqueous and organic phases by decantation.

GC/MS Conditions

A Varian 3900 gas chromatograph (GC) coupled to a Varian Saturn 2100T ion trap mass spectrometer (MS) (Varian, France) was used. The column was a 30 m $\times$ 0.25 mm, 0.25 μm CP-Sil 8 CB Low Bleed MS capillary column (Varian, France). Oven temperature was 80°C for 3 minutes then programmed from 50°C to 250°C at 3°C/min, then held at 250°C for 40 min. Helium as carrier gas at 1 ml/min was used. The extract samples were injected via a Varian CP-8400 autosampler fitted with a 5 μl syringe. Transfer line temperature was 280°C. Electron impact mass spectra were obtained at 70 eV ionization potential and peak identity was identified by NIST 2002 Data library.

Scanning Electron Microscopy

A Philips-FEI Quanta 200 ESEM/FEG Scanning Electron Microscopy operated at 20 kV, with a detector of secondary electrons Everhardt-Thornley, was used to image the control sample and some treated maritime pine needles. To improve the quality of the SEM images, a high vacuum was achieved.

Experimental Design

A central composite rotatable design was developed to evaluate effects of processing pressure (P) and processing time (t). The design needed 13 experiments

with eight (2^2) factorial points, four extra points (star points) to form a central composite design and five replications for the central point. The experiments were run in random order to minimize effects of unexpected variability due to extraneous factors. In the full factorial design, processing pressure (P) values varied between 1.5 and 5.5 bar and processing time (t) between 4 and 20 minutes (Table 1). Variables were codified in the way that their values ranged between $-\alpha$ and $+\alpha$ (α =.414), taking as the central point zero. Thus, $P^* =$ (P-3.5)/2 and $t^* =$ (t-12)/8; where P, t are the actual values and P^*, t^* the coded values of processing pressure and processing time. To avoid thermal reactions we limited the maximum processing pressure to 6.3 bar, corresponding to a temperature of 160°C.

Table 2 shows the central composite design matrix, with variables in both coded/noncoded forms. Data were adjusted to response surfaces, which were obtained by using *analysis design* procedure of 5.1 version *Statgraphics Plus for Windows* software.[17]

$$\eta = a_0 + a_1P + a_2t + a_{12}Pt + a_{11}P^2 + a_{22}t^2$$

where η is the considered response and a_0 is the value of the objective function in the central point conditions. a_1 and a_2 represent the principal effects associated

Table 2. Experimental design and results of global extraction yield and extraction yield of the different compounds

	Independent variables		Responses			
Runs	x_1	x_2	Yield	1	2	3
1	–1	–1	0.16	45.89	13.43	1.67
2	–1	+1	0.81	27.93	17.63	2.56
3	+1	–1	1.22	34.56	22.47	4.36
4	+1	+1	1.74	25.28	22.54	4.21
5	0	$-\alpha$	0.01	50.30	12.80	2.12
6	0	$+\alpha$	1.54	19.25	21.49	2.57
7	$-\alpha$	0	0.34	28.72	12.22	1.88
8	$+\alpha$	0	2.18	16.35	24.30	4.48
9	0	0	1.71	20.68	20.78	2.42
10	0	0	1.68	20.12	19.98	2.55
11	0	0	1.60	21.00	19.85	2.24
12	0	0	1.65	20.25	20.14	2.78
13	0	0	1.71	20.66	20.16	2.55
Mean absolute error for the 5 replications			0.05	0.31	0.32	0.17

(1): α-pinene, (2): β pinene, (3): germacrene D. The extraction yield is expressed in g of isolated oil/100 g d.m and the different compounds are expressed in g of constituent/100 g of isolated oil.

to the two variables. a_{12} represents the crossed effect among the variables and a_{11}, a_{22} represent the quadratic effects of the two studied variables. Thus, the model coefficients reflected the linear, quadratic, and interactive effects.

RESULTS AND DISCUSSION

To evaluate the effect of drying (in an oven at 25°C) on the composition of the essential oil extract, extraction by steam distillation was carried out on three samples of maritime pine needles, the first on fresh moist product, the second on needles dried to 40% moisture content (d.b.), and the third on needles dried to 10% moisture content. The results are grouped in Table 3. It appears that the extraction yield decreases at lower moisture content. For the most important compound, α-pinene, the yield decreased from 40.5% for fresh needles to 22.5% (g of / 100 g isolated oil) for needles dried to 10% moisture content (d.b.). This may be due to some evaporation of the compound during drying. Thus, for

Table 3. Percentage oil composition of fresh and dried *Pinus pinaster* needles oil isolated by steam distillation

	Fresh (63% d.b)	Dried (40% d.b)	Dried (10% d.b)
Yield Constituents	0.82	0.53	0.41
Tricyclene	0.08	0.059	0.06
α-Pinene	40.50	28.91	22.52
camphene	0.75	0.863	0.640
β-pinene	25.42	15.52	13.32
β-myrcene	3.61	1.571	1.012
p-cymene	4.02	0.015	0.014
limonene	3.52	2.994	2.424
γ-terpinene	0.08	0.141	0.175
dehydro p-cymene	0.07	0.033	0.021
terpinolene	0.74	0.902	0.765
4-terpineol	0.21	0.085	0.064
α-terpineol	1.05	0.735	0.413
α-copaene	0.40	1.005	0.912
longifolene	1.92	3.114	4.853
β-caryophillene	6.30	6.748	9.882
α-humulene	1.08	1.496	1.801
germacrene-D	3.21	2.328	1.758
g-cadinene	1.09	1.775	2.059
caryophillene oxyde	0.29	1.503	1.295

The percentages of the different constituents are expressed in g of constituent /100 g of isolated oil while the global yield is expressed in g of isolated oil/g of raw material (d.b).

extraction by instantaneous controlled pressure drop process the needles were treated in fresh state (∼63 % d.b.).

The results obtained following the experimental design are grouped in Table 3. The validity of the results was confirmed by the low uncertainty limit in the extraction yield (based on low error estimate) obtained from five replications at processing pressure of 3.5 bar and processing time of 12 minutes.

Fitting the Models

A regression analysis was carried out to fit mathematical models to the experimental data aiming at an optimal region for the responses studied. The predicted models can be described by Table 4 in terms of coded values. The significance of each coefficient was determined using Fisher test (F-value) and the probability p (p-value) in Table 5, which displays the variance analysis of the system (ANOVA). Corresponding variables would be more significant if absolute F-value becomes greater and p-value becomes smaller. It can be seen for all responses that processing pressure and processing time have a strong linear effect. For yield of isolated oil, a significant ($p < .05$) quadratic effect of processing time was also observed, indicating that the yield increases with the processing time up to a certain value beyond which a diminution is observed due to thermal degradation. For a processing pressure fixed at its central value, this time corresponds to 15 min. α-pinene and β-pinene exhibited a significant quadratic effect of processing time. The results suggest that changing in processing pressure or time had a highly significant effect on the yield of isolated oil and of the three selected compounds. The coefficients of determinations of models were also given in an ANOVA table (Table 5). They were systematically higher than 92% for the four models suggesting a good fit; the predicted models seemed to reasonably represent the observed values. Thus the responses were sufficiently explained by the models.

Table 4. Regression coefficients of the second-order polynomial equations

	Responses variables			
Regression coefficient	Yield	α-pinene	β-pinene	Germecrene D
a_0	1.670	20.542	20.182	2.508
a_1	1.137	−7.868	7.758	2.004
a_2	0.825	−17.787	4.139	0.344
a_{12}	−0.071	4.340	−2.065	0.520
a_{11}	−0.435	4.372	−1.264	0.890
a_{22}	−0.921	16.613	−2.379	0.056

Table 5. Analysis of variance showing the effect of the two independent variables (x_1, x_2) as a linear term, quadratic term, and interactions (cross product) on the responses

Source	DF	Sum of square	F-ratio	p-value
Yield				
P	1	2.58	90.62	<0.0001
t	1	1.36	47.71	0.0002
P^2	1	0.33	11.54	0.0115
T^2	1	1.47	51.66	0.0002
Pt	1	0.01	0.17	0.6890
Total error	7	0.21	—	—
R^2		0.959		
α-pinene				
P	1	123.28	10.56	0.0141
t	1	632.81	53.95	0.0002
P^2	1	33.25	2.84	0.1361
T^2	1	479.98	40.92	0.0004
Pt	1	18.83	1.61	0.2456
Total error	7	82.11	—	—
R^2		0.939		
β-pinene				
P	1	120.38	63.67	0.0001
t	1	34.27	1813	0.0038
P^2	1	2.78	1.47	0.2646
T^2	1	9.84	5.21	0.0565
Pt	1	4.26	2.26	0.1769
Total error	7	13.23	—	—
R^2		0.927		
Germacrene D				
P	1	8.03	94.33	<0.0001
t	1	0.23	2.78	0.1394
P^2	1	1.37	16.20	0.0050
T^2	1	0.00	0.06	0.8083
Pt	1	0.27	3.17	0.1180
Total error	7	0.59	—	—
R^2		0.943		

Response Surfaces for Yield of Isolated Oil

The regression models displayed in Table 4 allowed the prediction effect of the two processing parameters of D.I.C. isolation process. The relationship between independent and dependant variables can be illustrated in three-dimensional representations of the response surfaces generated by the models (Figures 1 and 2).

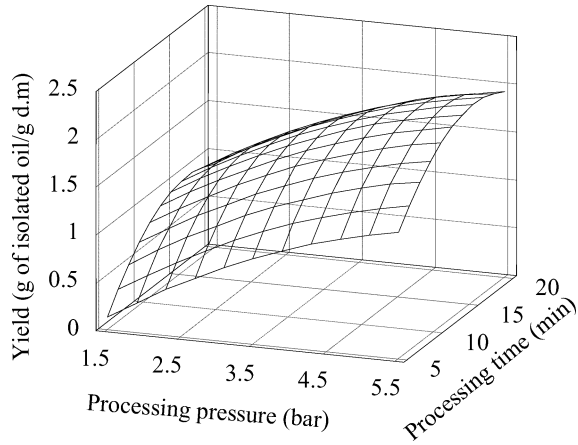

Figure 1. Response surface for the effect of processing pressure and processing time on the yield of isolated oil.

Figure 1 shows that both processing pressure and time demonstrated a significant linear increase on yield of isolated oil with the strongest effect for processing pressure. When processing pressure increases from 1.5 to 5.5 bar, extraction yield increases from 0.2 to 1.8% according to processing time. Figure 2 shows that it is possible to obtain a high yield at low processing times but at high processing pressures (>4–5 bar). This indicates that the mechanical strain induced by the rapid decompression and the brutal vaporization of water have two main effects: the dehydrating effect due to vaporization and a subsequent change in the surface tension of the glandular wall, causing it to crumble or rupture more readily. Similar effects were pointed out by Pare et al.,[18] for microwave extraction. The authors reported that an explosion at cell level occurred as a consequence of the sudden temperature rise generated by microwaves. The same observation was cited by Spiro and Chen,[19] who reported that the oil synthesized in the secretory cells was not released unless an external factor damages the gland. This observation was also verified by Boutekedjiret et al.,[20] who compared the isolation of rosemary oil by different extraction processes, including the Instantaneous Controlled Pressure Drop Process. The microstructure of the maritime pine needles is shown in Figure 3 where it can be seen that the size of pores increased with the severity of the thermomechanical extraction. The results also show that compared with other "flash" extraction processes, extraction by D.I.C. is more efficient because a high extraction yield can be obtained at low processing times. It should be noted that steam distillation at industrial scale is performed in 2 hours from 3 hours. Chen and Spiro,[21] who worked on microwave extraction of essential oil from rosemary leaves, reported that a long time at high temperatures could cause rearrangement or polymerization of some rosemary oil constituents that

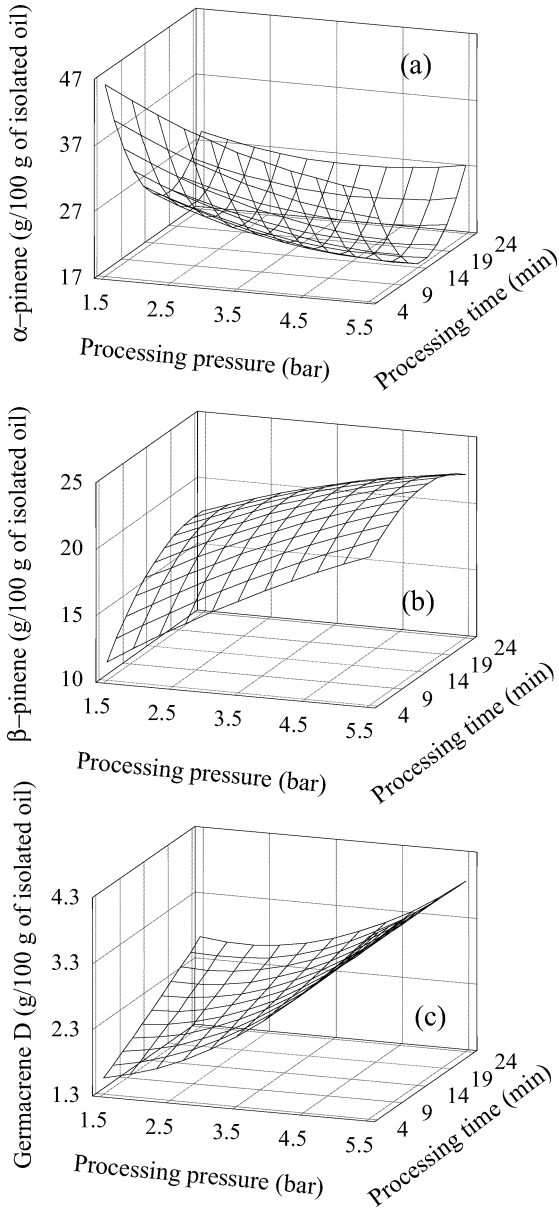

Figure 2. Responses surfaces showing the effect of processing steam pressure and processing time on the three studied compounds.

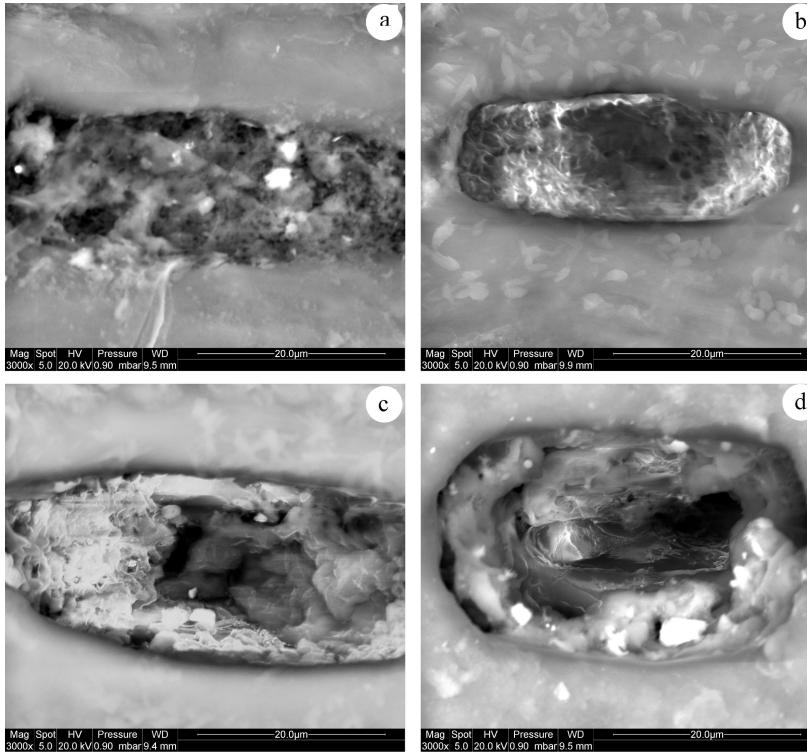

Figure 3. Scanning electron microscopy on the surface of untreated needles (a) and those of run 5 (b), run 6 (c), and run 4 (d).

are close to the constituents present in the needles of maritime pine oil. At 4.5 bar processing pressure, 10 minutes are sufficient to extract more than 80% of available essential oil. The maximum of extraction yield is almost reached after 15 minutes processing time. Beyond this value, a certain degradation expressed by a more deepened coloring of oil was observed. By looking at Figure 1 more closely, we can observe that the yield evolution versus processing time show a very rapid increase during the first minutes of isolation process, then gradually levelled to equilibrium value at the end of the process. Isolation of oil from maritime pine needles by instantaneous controlled pressure drop process seems to be regulated by two distinct phenomena corresponding to two steps. The first one is rapid compared to the second and corresponds to a free diffusion phenomenon, which takes place at the plant surface.

The oil recovered in the second step is probably regulated by osmosis phenomena and slow diffusion through the plant cells toward the surface. However, it can be seen that the oil collected in the last step ($\sim$5%) is very low compared to the one collected in the first step ($\sim$95%). It is obvious that

the major part of the oil is recovered by a simple process of free diffusion and evaporation. The proportions of these two parts for steam distillation extraction are generally lower for the first step and higher for the second. This difference may be attributed to the presence of saturated steam under pressure in the case of instantaneous controlled pressure drop process that allows reaching more endogenous sites than at atmospheric pressure in the case of steam distillation.

Response Surfaces for the Amounts of the Three Studied Compounds

From an industrial point of view, the qualitative criterion of maritime pine extracts is based on presence of three compounds, namely α-pinene, β-pinene, and germacrene D, in defined percentage in the essential oil as commercial standards. The α-pinene must represent between 33 and 43% of isolated oil, β-pinene between 22 and 32%, and germacrene D between 0.5 and 4%. For this reason, the effect of processing pressure and time on the quantity of these compounds was studied. Figure 2(a) represents the three response surfaces displayed by generated models for the three compounds. For α-pinene, the strongest effect is that of processing time followed by a visible quadratic effect of processing time whatever the processing pressure, suggesting that a large part of this compound is located on the surface of the naturally broken glands (exogenous sites) and are easily extracted according to a free diffusion phenomenon on the plant surface. Moreover, the decreasing of the quantity of α-pinene clearly indicates a certain degradation of this compound, which is more volatile. Comelli et al.[22] reported the same behavior for the isomerization reaction of α-pinene, which produces bicyclic and monocyclic compounds and other products, in presence of catalyst and temperature. For all selected processing times, the quantity of α-pinene decreased strongly up to 15 minutes and then stabilized. For β-pinene, which is also an important compound in the maritime pine needles oil, it can be seen from Figure 2(b) that the two processing parameters have a strong positive effect. The strong effect of processing time is more visible for the low values of processing pressure ($<$3.5 bar). For the highest processing pressures ($>$3.5 bar) a high percentages of β-pinene can be obtained but the evolution with the processing time is weak. Thus, at 4 bar, 4 minutes are sufficient to extract more than 90 % of this compound. The difference with the first studied compound (α-pinene) for which the strongest effect was processing time, is that for β-pinene the strongest one is the processing pressures, suggesting that β-pinene is not easily extractible as α-pinene and that it's probably located in endogenous storage sites of essential oil.

The same trend is observed for germacrene D for which the strong effect was that of processing pressure followed by its quadratic effect. From Figure 2(c), it can be seen that the quantity of this compound is stable between 1.5 and 1.8 g of germacrene D/100 g of isolated oil for processing pressures ranged between 1 and 3 bar. Over this value, the yield of germacrene D increases.

We can therefore argue that the proposed process is selective. If we favor the presence of α-pinene, it would be better to work at processing pressure included between 1.5 and 2.5 bar. In contrast, for β-pinene and germacrene D, processing pressures more than 4 bar are more suitable.

CONCLUSION

The empirical models developed for the yield of extracted oil and three studied compounds demonstrated a good agreement between the predicted values and actual values ($R^2 > .92$). Both processing pressure and time have a significant effect on yield of isolated oil and on the quantities in the three studied compounds. The results showed that for the lower processing times an appreciable yield can be obtained. However, in the present work, the domain of the processing pressure appears to be restrictive and in a further study, it could be advantageously extended.

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