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## Extraction process of the *Achyrocline satureioides* (Lam) DC. essential oil by steam distillation: modeling, aromatic potential and fractionation

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### ABSTRACT

The essential oil of *Achyrocline satureioides* was obtained by steam distillation in four operating conditions (1.0, 1.5, 2.0 and 2.5 bar) and the aromatic profile of these essential oils was evaluated by gas chromatography/olfactometry (GC/O). It was observed that the relation between the aromatic intensities and the compounds concentration is not directly proportional, except for the  $\alpha$ -pinene, which presented a high concentration and aromatic intensity. The essential oil compounds were identified by gas chromatography/mass spectrometry and a principal component analysis (PCA) was used to evaluate the pressure effect on the essential oil composition. Through the PCA, similarity of composition was observed between pressures of 2.0 and 2.5 bar. Furthermore, a mathematical modeling of extraction process and an essential oil theoretical fractionation process study by batch distillation of the major compounds were performed. In order to enhance its aromatic activity, the simulation methodology applied to fractionate the *A. satureioides* essential oil presented a high-purity (99.10%)  $\alpha$ -pinene fraction.

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## 1 Introduction

The species *Achyrocline satureioides* (Lam) DC., popularly known as marcela, is native to southeastern South America and grows on sandy or rocky soils, in hilly and simple terrain. It is common in Brazil, Uruguay and Argentina (1,2), among other 40 species of *Achyrocline*, most of which are from tropical and sub-tropical America and some from tropical Africa and Madagascar (3). Lamaty et al. (4) and Cezarotto et al. (5) have reported studies on the composition of the essential oil of *Achyrocline satureioides*, where the compounds  $\alpha$ -pinene and (E)-caryophyllene were the most abundant components. Other works for this essential oil include the use as a repellent agent for insects (5,6), antioxidant agent (7) and antimicrobial agent (8).

Vargas et al. (9) presented a descriptive analysis of aromatic properties of the *A. satureioides* extracts, obtained by CO<sub>2</sub> supercritical, based on the detection and description of their sensorial aspects, while Retta et al. (10) evaluated and validated the *A. satureioides* and *Helicrysum italicum* extracts aromas as a potential perfume ingredient. It is also observed that the marcela extracts are used in several products marketed in the MERCOSUR region for their characteristic complex, bitter, aromatic flavor (11). Flavored compounds are widely used in the manufacture of perfume, foods, beverages,

cosmetics, detergents, chemicals and pharmaceuticals, among other products (12). The growing market for flavorings aims to influence consumers in relation to sensory properties or simply to make the product easily recognizable (13).

The chemical analysis of the essential oils by GC/MS is traditionally followed by a statistical analysis using the principal component analysis (PCA), in order to evaluate its similarities and differences. However, only the use of gas chromatography is not sufficient when there is a global interest in fragrances and odors of a sample. According to Van Ruth (14), only a small part of the large number of volatile compounds that occur in a fragrant matrix contributes to the perception of its odor. In addition, the contribution of the compounds is not equivalent to the overall flavor profile of a sample. Thus, a large peak area in the gas chromatography, generated by a chemical detector, does not necessarily correspond to high odor intensities. Grosch (15) and Rowe (16) report that compounds present in minimal amounts could be more important contributors than those present at higher concentrations. A more adequate solution for these questions is the use of gas chromatography/olfactometry (GC/O), since it allows the evaluation of the odor (active components of complex mixtures) through the direct correlation with the chromatographic peaks of interest (17).

The present work aimed to evaluate the extraction process pressure effect on the composition and aromatic potential of the *Achyrocline satureioides* essential oils obtained by steam distillation. In order to verify the similarity of the essential oils, they were analyzed by GC/MS and GC/O, and the PCA technique was applied to the data. Also, a model based on the principles of mass transfer was used to represent the extraction data obtained experimentally, aiming at a possible scale-up procedure (18). On the other hand, the fractionation of essential oils has already proved effective as a way to potentiate its active properties (19,20). In this way, a theoretical study was used conducted to simulate the rectification process for the essential oil major compounds by batch distillation (21), in order to obtain enriched fractions of the compounds with high aromatic potential.

## 2 Materials and methods

### 2.1 Plant material

The plant material used in the experiments was collected and identified by Jose Valdeci Oliveira da Silva in Santo Antônio da Patrulha—Brazil (−29.82, −50.52) on March 2015. The raw material consists of the dry aerial parts of *A. satureioides* (Lam.) DC., composed of inflorescences and branches. The material was stored at room temperature (22–25°C). Only the inflorescences of the plant material were used for the steam distillation process. To determine the *A. satureioides* specific mass, it was initially determined the mass of the sample and the actual volume of each sample was determined using the gas pycnometry technique (22) with the use of a multipycnometer (Quantachrome). A sample of marcela inflorescence (1 g) was used to quantify its humidity (thermogravimetric balance—BEL Engineering).

### 2.2 Extraction of essential oil by steam distillation

Extractions of the essential oils of *A. satureioides* were carried out in a pilot-scale equipment (23) which has a boiler with a capacity of 20 L (electric resistor—2 kW), a extraction vessel (bed height of 31.5 cm and diameter of 19.0 cm), a heat exchanger and a liquid-liquid separator. The extractions were performed in triplicate, in four different absolute pressures: 1.0, 1.5, 2.0 and 2.5 bar. The mass of plant material used in each and all extractions was 600 g and the experimental points to build the extraction curve were obtained at 5 min intervals. The extraction step is ended when the volume change of essential oil in the separator is not observed by three consecutive measurements.

### 2.3 GC/MS analysis

Samples of the essential oil extracted by steam distillation were first submitted to a dehydration pretreatment by the addition of anhydrous sodium sulfate and diluted in cyclohexane (Merck P.A.) in the ratio 1:10 (v/v). For the essential oil identification, analysis was performed on an Agilent gas chromatograph, model 7890A coupled to an Agilent 5975C mass spectrometer (GC/MS). The analytical column was a silica capillary column HP-5MS (30 m × 0.25 mm, 0.25 μm). The method used in the GC/MS analysis was as follows: oven column temperature, 60°C for 8 min, increasing to 180°C with 3°C/min; 180°C–250°C with 20°C/min; and then it was kept at 250°C for 10 min. The injector temperature was kept at 250°C. The volume injected was 0.2 μL in split mode, with a 1:55 split ratio. The carrier gas was helium with a 0.8 mL/min flow rate (24).

The identification of the compounds was performed by comparing their retention indexes in the column used, determined from a series of n-alkanes (C8–C20), with those of pure standards. To confirm the identity of the compounds, a comparison of the mass spectra was also carried out (25).

### 2.4 GC/O analysis

The olfactometric profile analysis of the essential oils samples was performed by gas chromatograph equipped with two detectors: flame ionization detector (FID) by Perkin Elmer Auto System and sniffing port (26). In the olfactory detector, the transfer section has a temperature control so that each component that elutes the GC column reaches the olfactory cone without condensation losses on the walls of the capillary. The same column and method used for the GC/MS characterization were used for this analysis in the GC/O, thus allowing the relationship between the results of the sensorial analysis and the chemical composition of the essential oil. The olfactometer was maintained at 250°C throughout the analysis. For the essential oil GC/O analysis, 1 μL of the sample was injected. In order to perform the *Achyrocline satureioides* essential oil olfactory analysis (GC/O), four evaluators were selected. Each of the evaluators reported the following information on the aromas during the analysis: time in relation to the beginning of the analysis in which a certain aroma was perceived, aroma description according to the aroma description wheel described by McGinley et al. (27), and intensity of the aroma in a scale of integers, from 1 to 5, with 1 being the lowest intensity and 5 being the highest intensity.

From the data provided by the evaluators, it is possible to calculate the modified frequency (MF)

(Equation 1). According to Dravnieks (28), MF is defined as a magnitude that correlates the intensity and frequency of detection of an analyzed sample.

$$MF(\%) = \sqrt{F(\%)I(\%)} \quad (1)$$

where  $F(\%)$  is the frequency of detection of a flavor between the universe of evaluators and  $I(\%)$  is the average intensity of a flavor attribute in relation to the scale, being 100% corresponding to the average 5. Hundred percent MF corresponding to an aroma detected by all the evaluators with the maximum intensity.

## 2.5 Principal component analysis (PCA)

The objective of PCA use is to compare the compositions of the essential oils of *A. saturoioides* extracted at different pressures by steam distillation and group them in terms of similarity (29). The software used to perform the statistical analysis was MINITAB 16, requiring the values of area percentage of each essential oil component. With these data, the software calculates the covariance matrix along with the new variables, called main components. According to the definition of the PCA calculation, the total of the new variables will be, necessarily, one less than the number of cases. Since there were four pressure conditions analyzed in this work, the number of main components in this work is three.

## 2.6 Mathematical modeling

A dynamic model was used for the mathematical representation of the extraction process. Based on the model proposed by Reverchon (18), it consists of a one-dimensional mass balance for the extract, considering the hypothesis of a linear behavior for the solid-fluid phase equilibrium. The mass balance model proposed was developed considering negligible axial dispersion, density, solvent flow rate are constants throughout the bed, and considering that the essential oil can be assumed as a single pseudocompound.

The distribution of the pseudocomponent in the fluid and solid phases is obtained through the mass balance in the column. Neglecting the radial dispersion along the column, and considering only two independent variables, the time ( $t$ ) and the fixed bed height ( $z$ ), the model was developed. It is assumed that at the beginning of the process the concentration of oil in the aromatic plants is homogeneous and equally distributed throughout the bed. Based on the assumptions listed above, the mass balance in the solid and fluid phases is given below (Equations 2 and 3) (18).

Mass balance in the vapor phase:

$$\frac{\partial C(z, t)}{\partial t} = -v \frac{\partial C(z, t)}{\partial z} - \frac{1 - \varepsilon}{\varepsilon} \rho_s \frac{\partial q(z, t)}{\partial t} \quad (2)$$

Solid phase mass balance:

$$\frac{\partial q(z, t)}{\partial t} = -k_{TM}[q(z, t) - K \cdot C(z, t)] \quad (3)$$

Where  $C(z, t)$  is the essential oil concentration in the vapor phase;  $q(z, t)$  is the concentration of oil in the aromatic plant;  $v$  is the interstitial vapor velocity;  $\varepsilon$  is the porosity of the bed;  $k_{TM}$  is the internal mass transfer coefficient;  $\rho_s$  is the specific mass of the aromatic plant and where  $K$  is the equilibrium constant between the phases. The resolution of the model also considers the following initial and boundary conditions.

$C(z, 0) = 0$  and  $q(z, 0) = q_0$ , being  $q_0$  the total amount of extract present in the solid phase (experimental extraction yield), and  $C(0, t) = 0$  as boundary condition. The linear behavior for the solid-fluid phase equilibrium is represented by  $q^*(z, t) = K \cdot C(z, t)$  (18,30).

The simulation of the *A. saturoioides* extraction process was carried out in the software EMSO (Environment for Modelling, Simulation and Optimization), which is an equation-oriented simulator suitable for dynamic simulations (31). The internal mass transfer coefficient  $k_{TM}$ , and the equilibrium constant  $K$ , were estimated by least squares method and the objective function minimized by the Nelder-Mead algorithm (32). This software also provides the statistical analysis through the parameter correlation obtained from the variance and covariance matrixes.

## 2.7 Essential oil fractionation

In order to perform a rectification process simulation of the major compounds (compounds with strong aromatic potential) present in the *A. saturoioides* essential oil, the batch distillation methodology, involving several steps, developed by Almeida et al. (21), was applied. The method used to calculate the vapor pressure of the compounds of interest was the CSGC-PRV (33), based on the critical properties, obtained through the contribution of each functional group, and the modified Raoult's law was used to calculate the phase equilibrium.

The dynamic model was implemented in the generic process simulator EMSO (31) along with the thermodynamic package of the industrial process simulator iiSE. The simulator is able to solve the system with any set of given conditions, and for this distillation process simulation the same conditions indicated by Almeida et al. (21), were used: 18 equilibrium stages, total column holdup (amount of material that accumulates in the column) of

5%, constant reflux ratio equal to 8, initial charge of essential oil in the boiler is 10 mol, with a heating power of 200 W and the system pressure is set to 75 mmHg or 10 kPa.

### 3 Results and discussion

#### 3.1 Essential oil: extraction and analysis

The experimental values of marcela essential oil total yield obtained at 1.0, 1.5, 2.0 and 2.5 bar were  $0.082 \pm 0.002 \text{g}_{\text{oil}}/100\text{g}_{\text{plant}}$ ,  $0.061 \pm 0.003 \text{g}_{\text{oil}}/100\text{g}_{\text{plant}}$ ,  $0.069 \pm 0.002 \text{g}_{\text{oil}}/100\text{g}_{\text{plant}}$ ,  $0.074 \pm 0.004 \text{g}_{\text{oil}}/100\text{g}_{\text{plant}}$ , respectively, while the specific mass of the vegetal material, and essential oil obtained experimentally were  $\rho_{\text{vegmat}} = 1.29 \text{ g/mL}$  and  $\rho_{\text{oil}} = 0.78 \text{ g/mL}$ . The experimental humidity of the marcela inflorescences used to obtain essential oil was of 7.8% and the bed porosity, calculated from extraction vessel volume and vegetal material volume, was of 0.891.

The percentages of each component for marcela essential oil obtained by GC/MS are presented in Table 1. The major compounds obtained at pressures of 1.0, 1.5, 2.0 and 2.5 bar, respectively, are: E-caryophyllene: (29.70%; 31.06%; 26.60% and 26.49%),  $\alpha$ -pinene (23.59%; 9.63%; 11.73% and 10.07%),  $\alpha$ -copaene (6.64%; 8.81%; 7.76% and 6.56%) and  $\alpha$ -humulene (5.06%; 4.79%; 4.48% and 7.25%). These major constituents found for the essential oil of *A. saturoioides* are in agreement with those found in studies conducted by Lorenzo et al. (1) and Vargas et al. (9).

The evaluation of different extraction pressures aimed the identification of its influence in the essential oil yield and its composition variation, assuming that the steam generated in the boiler is saturated, it is known that the higher the system pressure, the higher the extraction temperature. The use of higher pressures and temperatures in the extraction could increase the solubility of the higher molecular mass compounds of the essential oil in the water vapor and thereby increase the yield of the process. In the case of the essential oil of *A. saturoioides*, the extraction pressure influenced the composition of the essential oil, but not proportionally to the increase in pressure.

From the PCA use, the mathematical procedure that uses an orthogonal transformation to convert a set of possibly correlated variables into a set of linearly uncorrelated variables; it was possible to interpret and correlate the marcela essential oil obtained at different pressures. The PCA statistical analysis indicated that 99.6% of the total variance of the data was represented by the two main components. In Figure 1, it was observed the behavior of the *A. saturoioides* essential oil

composition related to the variation of the extraction pressure and its relation with the compounds. Five compounds stood out from the others,  $\alpha$ -pinene,  $\alpha$ -humulene,  $\alpha$ -copaene,  $\delta$ -cadinene and E-caryophyllene. The compounds  $\alpha$ -humulene,  $\alpha$ -copaene,  $\delta$ -cadinene and E-caryophyllene present similar concentration in the marcela essential oils extracted at four pressures studied, but the high concentration of  $\alpha$ -pinene in essential oil obtained at 1.0 bar justifies the difference among the essential oil extracted at 1.0 bar and the essential oils extracted at 1.5 and 2.5 bar (Figure 1). This difference occurs because the lower the pressure condition implies the lower the temperature during the extraction and consequently the more volatile compounds are extracted in this condition thereby providing richer extract in these compounds.

The GC/O analysis with *A. saturoioides* essential oil identified a total of 22 aromas with MF greater than or equal to 40, being five aromas in the sample of 1.0 bar, eight in the 1.5 bar, four at 2.0 bar and five at 2.5 bar, as shown in Table 2. According to the literature (32), MF (Equation 1) below 40 reflect low-intensity aromas and/or evaluators with less olfactory sensitivity than others. Among the identified aromas stand out smoked and floral refreshing, because they were identified in the four pressures studied. The putrid, rust, herb and floral aromas were identified in two pressures. Regarding the extraction pressure, it is observed that the pressure of 1.5 bar was the condition that presented the highest number of aromas detected. In this context, it is clear that the extraction pressure influenced the aromatic profile of the marcela essential oil, but this behavior is not proportional to the pressure variation. Thus, Figure 2 shows the aromas with MF greater than or equal to 40 for pressures of 1.0, 1.5, 2.0 and 2.5 bar, respectively.

Comparing the GC/MS and GC/O identification, only four compounds,  $\alpha$ -pinene,  $\alpha$ -terpineol,  $\alpha$ -copaene and isodene, were detected by both methods. This result demonstrates that not all major compounds detected in GC/MS are obtained in the sensory analysis with MF greater than or equal to 40. Only the  $\alpha$ -pinene compound is among the major components in both methods. This behavior confirms the literature (14,15) which describes that the compounds do not contribute equally to the aroma profile of a sample, that is, high relative concentration of a compound identified by a chromatograph, does not necessarily correspond to the high intensity of aroma.

#### 3.2 Fractional batch distillation

The simulation for the essential oil fractionation process can be applied to mixtures with different compounds, resulting in different distillate and temperature profiles



**Table 1.** GC/MS chromatographic analysis of *Achyrocline satureioides* essential oil extracted at four different pressures.

Compound <sup>a</sup>	LRI <sub>t</sub> <sup>b</sup>	LRI <sub>e</sub> <sup>c</sup>	%Area <sup>d</sup>			
			1.0 bar <sup>e</sup>	1.5 bar	2.0 bar	2.5 bar
α-Pinene	932	933	<b>23.59 ± 0.24</b>	<b>9.63 ± 0.90</b>	<b>11.73 ± 0.67</b>	<b>10.07 ± 1.90</b>
Camphene	946	946	0.07 ± 0.03	0.17 ± 0.15	0.31 ± 0.03	0.24 ± 0.11
β-Pinene	974	974	0.36 ± 0.50	0.38 ± 0.33	0.49 ± 0.03	0.45 ± 0.21
Myrcene	988	991	–	0.12 ± 0.11	0.14 ± 0.03	0.13 ± 0.07
α-Terpinene	1014	1016	–	0.03 ± 0.03	–	0.02 ± 0.03
o-Cymene	1022	1024	–	0.17 ± 0.15	0.21 ± 0.07	0.15 ± 0.05
Limonene	1024	1029	1.17 ± 0.85	0.98 ± 0.89	1.63 ± 0.41	0.98 ± 0.22
1,8-Cineole	1026	1031	–	0.10 ± 0.13	0.21 ± 0.09	0.17 ± 0.21
(Z) β-Ocimene	1032	1041	0.38 ± 0.65	1.57 ± 1.36	1.60 ± 0.37	1.62 ± 0.84
(E) β-Ocimene	1044	1050	–	0.14 ± 0.12	0.14 ± 0.04	0.13 ± 0.07
γ-Terpinene	1054	1059	–	0.12 ± 0.11	0.16 ± 0.04	0.14 ± 0.05
Terpinolene	1086	1088	–	0.16 ± 0.14	0.23 ± 0.06	0.18 ± 0.03
n-Nonanal	1100	1105	–	0.04 ± 0.04	0.09 ± 0.08	–
endo-Fenchol	1114	1113	–	0.08 ± 0.07	0.11 ± 0.03	0.08 ± 0.01
Campholenal	1122	1126	–	0.07 ± 0.07	0.04 ± 0.04	0.03 ± 0.03
allo-Ocimene	1128	1130	–	0.04 ± 0.03	0.06 ± 0.05	0.03 ± 0.03
trans-Pinocarveol	1135	1138	–	0.05 ± 0.04	0.07 ± 0.06	0.03 ± 0.03
neo allo-Ocimene	1140	1142	–	0.05 ± 0.05	0.02 ± 0.03	0.06 ± 0.02
Camphene hydrate	1145	1147	–	0.04 ± 0.04	–	–
Pinocarvone	1160	1162	–	0.09 ± 0.09	0.05 ± 0.05	–
Borneol	1165	1165	–	0.08 ± 0.09	0.21 ± 0.08	0.14 ± 0.02
Terpinen-4-ol	1174	1177	–	0.07 ± 0.07	–	0.04 ± 0.03
α-Terpineol	1186	1191	–	0.07 ± 0.07	0.17 ± 0.06	0.12 ± 0.02
n-Decanal	1201	1207	–	0.02 ± 0.03	–	0.01 ± 0.02
Methyl myrtenate	1293	1297	–	0.02 ± 0.04	–	–
Isolatedene	1374	1373	–	0.18 ± 0.15	0.26 ± 0.04	0.28 ± 0.03
α-Copaene	1374	1379	<b>6.64 ± 1.32</b>	<b>8.81 ± 0.59</b>	<b>7.76 ± 0.35</b>	<b>6.56 ± 0.79</b>
Sativene	1390	1390	–	0.10 ± 0.08	0.16 ± 0.01	0.11 ± 0.03
Z-Caryophyllene	1408	1407	0.06 ± 0.11	0.15 ± 0.14	0.25 ± 0.04	0.20 ± 0.03
α-Gurjunene	1409	1410	–	0.33 ± 0.29	0.45 ± 0.03	0.34 ± 0.17
E-Caryophyllene	1417	1428	<b>29.70 ± 3.10</b>	<b>31.06 ± 2.30</b>	<b>26.60 ± 1.52</b>	<b>26.49 ± 2.83</b>
β-Gurjunene	1431	1431	–	0.21 ± 0.18	0.18 ± 0.15	0.17 ± 0.15
Aromadendrene	1439	1442	1.23 ± 0.61	1.25 ± 1.09	1.74 ± 0.33	1.60 ± 0.47
α-Humulene	1452	1457	5.06 ± 1.31	4.79 ± 0.77	4.48 ± 0.84	7.25 ± 1.76
E-β-Farnesene	1454	1460	–	0.13 ± 0.22	–	–
9-epi-E-Caryophyllene	1464	1463	1.20 ± 0.15	1.50 ± 0.13	1.46 ± 0.19	1.29 ± 0.34
4,5-di-epi-Aristolochene	1471	1470	–	0.02 ± 0.03	0.30 ± 0.21	0.11 ± 0.04
trans-Cadina-1(6),4-diene	1475	1475	–	0.40 ± 0.40	1.33 ± 0.64	0.20 ± 0.34
γ-Murolene	1478	1479	1.99 ± 0.37	2.13 ± 0.35	0.82 ± 1.09	2.45 ± 0.39
α-Amorphene	1483	1482	0.08 ± 0.14	0.16 ± 0.14	0.25 ± 0.25	0.26 ± 0.03
β-Selinene	1489	1488	1.09 ± 0.98	0.75 ± 0.67	1.08 ± 0.37	2.30 ± 0.69
δ-Selinene	1492	1493	–	0.13 ± 0.13	0.17 ± 0.04	0.14 ± 0.12
Vidiflorene	1496	1497	1.57 ± 0.64	1.64 ± 0.45	1.45 ± 0.48	2.48 ± 0.42
α-Murolene	1500	1503	1.86 ± 0.27	2.12 ± 0.35	1.81 ± 0.17	1.77 ± 0.27
α-Bulnesene	1509	1508	–	0.04 ± 0.07	0.11 ± 0.01	0.10 ± 0.02
γ-Cadinene	1513	1517	2.01 ± 0.38	2.24 ± 0.30	2.01 ± 0.17	2.14 ± 0.20
δ-Cadinene	1522	1524	7.70 ± 1.46	8.23 ± 0.81	8.22 ± 0.98	7.10 ± 1.14
trans-Cadina-1,4-diene	1533	1536	0.27 ± 0.47	0.65 ± 0.63	0.64 ± 0.22	0.55 ± 0.18
α-Calacorene	1544	1541	0.66 ± 0.12	0.42 ± 0.36	0.60 ± 0.04	0.55 ± 0.05
Selina-3,7(11)-diene	1545	1546	0.64 ± 1.11	0.88 ± 0.78	1.25 ± 0.21	1.36 ± 0.18
Silphiperfol-5-en-3-ol A	1557	1555	0.67 ± 1.17	0.69 ± 0.60	1.21 ± 0.19	1.08 ± 0.14
β-Calacorene	1564	1565	–	0.02 ± 0.03	–	–
Caryophyllenyl alcohol	1570	1573	0.82 ± 1.43	1.37 ± 0.62	1.25 ± 0.06	1.08 ± 0.16
Caryophyllene oxide	1582	1588	3.21 ± 2.80	3.47 ± 0.54	3.07 ± 0.09	1.83 ± 0.99
Viridiflorol	1592	1594	0.19 ± 0.34	0.12 ± 0.10	0.16 ± 0.03	0.17 ± 0.01
Cubeban-11-ol	1595	1596	–	0.15 ± 0.13	0.23 ± 0.01	0.26 ± 0.08
Humulene epoxide II	1608	1611	0.44 ± 0.08	0.22 ± 0.19	0.33 ± 0.05	0.49 ± 0.09
1,10-di-epi-Cubenol	1618	1620	0.51 ± 0.89	0.61 ± 0.53	0.99 ± 0.13	1.07 ± 0.12
1-epi-Cubenol	1627	1632	0.84 ± 1.46	1.46 ± 0.31	1.35 ± 0.10	1.26 ± 0.23
epi-α-Cadinol	1638	1645	0.82 ± 1.41	0.81 ± 0.71	1.27 ± 0.22	1.27 ± 0.24
α-Murolol	1644	1650	0.22 ± 0.39	0.21 ± 0.18	0.30 ± 0.02	0.26 ± 0.06
α-Eudesmol	1652	1653	–	0.08 ± 0.01	0.14 ± 0.06	0.16 ± 0.01
α-Cadinol	1652	1658	0.34 ± 0.58	0.39 ± 0.34	0.54 ± 0.20	0.73 ± 0.14
Cadalene	1675	1677	0.27 ± 0.47	0.25 ± 0.21	0.30 ± 0.07	0.21 ± 0.03
<b>Total identified</b>			<b>95.69</b>	<b>92.40</b>	<b>91.96</b>	<b>90.38</b>

<sup>a</sup>The identification of peaks is based on comparison between the experimental Linear Retention Index (LRI) data with those from literature (Adams, 2007).

<sup>b</sup>Theoretical Linear Retention Index (LRI<sub>t</sub>) on HP-5MS series (Adams, 2007).

<sup>c</sup>Experimental Linear Retention Index (LRI<sub>e</sub>) calculated in relation to n-hydrocarbons series reported according to their elution order on HP-5MS series.

<sup>d</sup>The values correspond to relative proportions of the constituents of essential oils that were expressed as percentages obtained by normalizing the peak area.

<sup>e</sup>Operational conditions in absolute pressure.

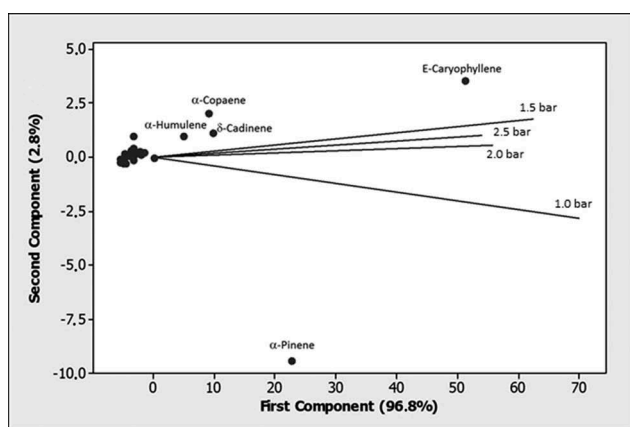


Figure 1. Variation behavior of the *A. satureioides* oil in relation to the different extraction pressures (1.0, 1.5, 2.0 and 2.5 bar).

Table 2. Compounds identified by GC/O of the *A. satureioides* essential oils.

Pressure	RI	Compound	% Area	Aroma <sup>b</sup>	MF (%)
1.0 bar	855	- <sup>a</sup>	-	Smoked	74
	933	$\alpha$ -Pinene	23.59	Refreshing floral	71
	985	-	-	Rust/Herbal/Floral	51
	1260	-	-	Burnt/Floral	45
	1530	-	-	Burnt/Erva	45
1.5 bar	806	-	-	Herbal/Burnt	40
	855	-	-	Smoked	84
	894	-	-	Herbal/Floral	51
	933	$\alpha$ -Pinene	9.63	Refreshing floral	64
	1191	$\alpha$ -Terpineol	0.07	Refreshing/Burnt/Herbal	64
	1211	-	-	Urine/Putrid	77
	1356	-	-	Floral/Sweet	51
2.0 bar	1375	$\alpha$ -Copaene	8.81	Herbal	55
	855	-	-	Smoked	77
	933	$\alpha$ -Pinene	11.73	Refreshing floral	55
	985	-	-	Rust/Herbal/Floral	43
	1373	Isoledene	0.26	Herbal/Burnt	40
2.5 bar	806	-	-	Herbal/Burnt	67
	855	-	-	Smoked	81
	933	$\alpha$ -Pinene	10.07	Refreshing floral	61
	1211	-	-	Urine/Putrid	67
	1394	-	-	Floral/Burnt	51

<sup>a</sup>Aroma detected in GC/O but not identified in GC/MS; <sup>b</sup>Aroma detected in GC/O.

according to their initial compositions. The number of components used in the simulation could increase the process complexity, due to the input required (pure components and mixture properties). The composition of the essential oil obtained in the 1.0 and 2.5 bar pressure was used, because these conditions presented the highest yields among the obtained data and presented the most significant difference in their compositions, as shown in Figure 1. Due to the great complexity of simulation with all the identified compounds, 14 representative constituents were used for 1.0 bar essential oil, which represent 90.7% of the total detected. For the 2.5 bar essential oil, 16 compounds were used, representing 89.5% of the total detected. The selected compounds are described in Tables 3 and 4, and had their composition normalized so that their sum is equal to unity.

Table 3 presents the results for the batch distillation simulation with the *A. satureioides* essential oil extracted at 1.0 bar pressure, in which three main cuts (MC) and two off-cuts (OC) were obtained. The recovery of cuts MC11, MC12 and MC13 in relation to the initial charge of essential oil in the reboiler is 26.5%, 6.7% and 50.8%, respectively. The recycle fractions, although they do not have the presence of a major substance, have the potential to be reprocessed in subsequent recycling batch cycles. The main fractions are rich in  $\alpha$ -pinene (99.10%),  $\alpha$ -humulene (77.16%) and E-caryophyllene (67.65%).

Table 4 presents the results for the batch distillation simulation with the *A. satureioides* essential oil obtained at 2.5 bar pressure, in which three main cuts (MC) and three off-cuts (OC) were obtained. The recovery of cuts MC21, MC22 and MC23 in relation to the initial charge of essential oil in the reboiler is 7.03%, 9.61% and 2.48%, respectively. The main fractions are also rich in  $\alpha$ -pinene (98.66%),  $\alpha$ -humulene (81.45%) and (Z)  $\beta$ -ocimene (77.63%). Mostly of the distillate (71%) is recovered as an off-cut (OC22) with high potential to be reprocessed as it contains 51.08% of E-caryophyllene.

Figure 3 shows the evolution of the distillate composition over time from the batch distillation process for the oil of *A. satureioides* for both conditions. The main-cuts and off-cuts are determined by the distillation column top temperature. Figure 4 presents the parallel between the top composition profile and the previously established temperature levels. The equilibrium temperature for each stage is determined by its thermodynamics and since the major compounds for the two simulated cases are the same, the temperature levels are also the same, but reached at different times.

According to Almeida et al. 2018, from a commercial point of view, essential oils and their rectified derivatives have a wide range of applications, such as aromatherapy, fragrance industry, cosmetics and perfumery. In these industries, essential oils are used much more for their organoleptic properties, such as taste and odor, than for their active properties. This makes the required purity in each product vary greatly according to its purpose. In this sense, the  $\alpha$ -pinene compound obtained with a purity of 99.10% and 98.66% could be directly placed to the market. The  $\alpha$ -humulene (77.16% and 81.45%) and E-caryophyllene (67.65% and 51.08%) fractions could be redirected to a new batch order to achieve a higher purity.  $\alpha$ -pinene is among the most used compounds in the flavor and fragrance industry and it has a high added value (34,35). This simulation, in terms of a theoretical study, demonstrates the suitable strategy of batch

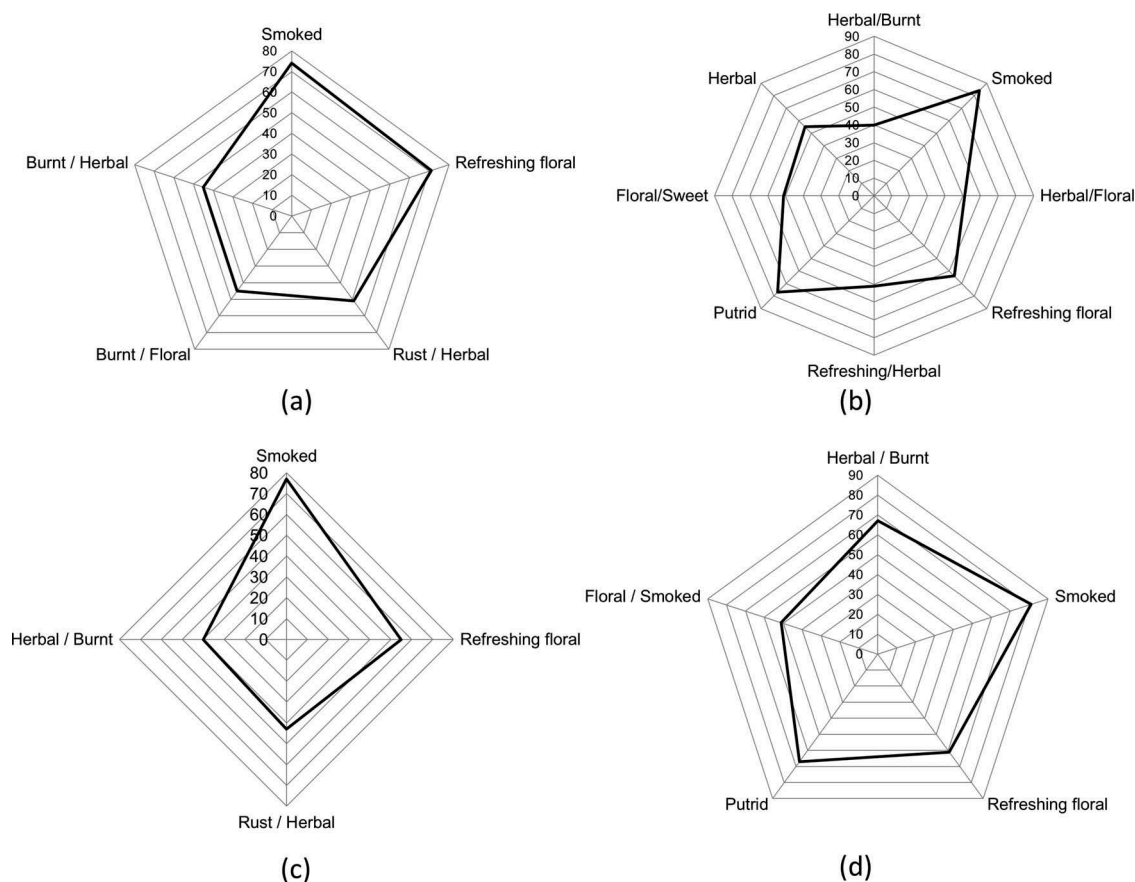


Figure 2. Sensory profile of *A. satureioides* essential oil. Essential oils extracted at 1.0 bar (a), 1.5 bar (b), 2.0 bar (c) and 2.5 bar (d).

Table 3. Molar fraction of the *A. satureioides* essential oil extracted at 1.0 bar and the main cuts obtained from the simulation of its fractionation process.

Constituents	Initial	MC1	OC1	MC2	MC3	OC2
E-Caryophyllene	0.348	–	–	–	<b>0.676</b>	0.077
$\alpha$ -Pinene	0.266	<b>0.991</b>	0.511	0.033	–	–
$\alpha$ -Humulene	0.057	0.001	0.321	<b>0.772</b>	0.005	–
$\beta$ -Pinene	0.004	0.008	0.099	0.011	–	–
(Z) $\beta$ -Ocimene	0.004	–	–	0.011	0.007	–
$\delta$ -Cadinene	0.087	–	–	–	0.046	0.459
$\alpha$ -Copaene	0.075	–	–	–	0.149	–
Caryophyllene oxide	0.036	–	–	–	–	0.084
$\gamma$ -Cadinene	0.045	–	–	–	0.033	0.206
$\alpha$ -Murolene	0.021	–	–	–	0.001	0.146
Vidiflorene	0.018	–	–	–	0.028	0.026
Aromadendrene	0.014	–	–	–	0.028	–
$\beta$ -Selinene	0.012	–	–	–	0.024	0.001
Limonene	0.013	–	0.069	0.173	0.002	–
<b>Recovery<sup>a</sup></b>		<b>26.5%</b>	<b>1.2%</b>	<b>6.7%</b>	<b>50.8%</b>	<b>14.2%</b>

<sup>a</sup>Recovery relative to the initial batch load (molar basis).

distillation to obtain a pure extract in  $\alpha$ -pinene using the *A. satureioides* essential oil.

### 3.3 Extraction modeling

The mathematical modeling of the marcela essential oil extraction process is aligned with the fractionation, since the joint action of these two calculation tools allows

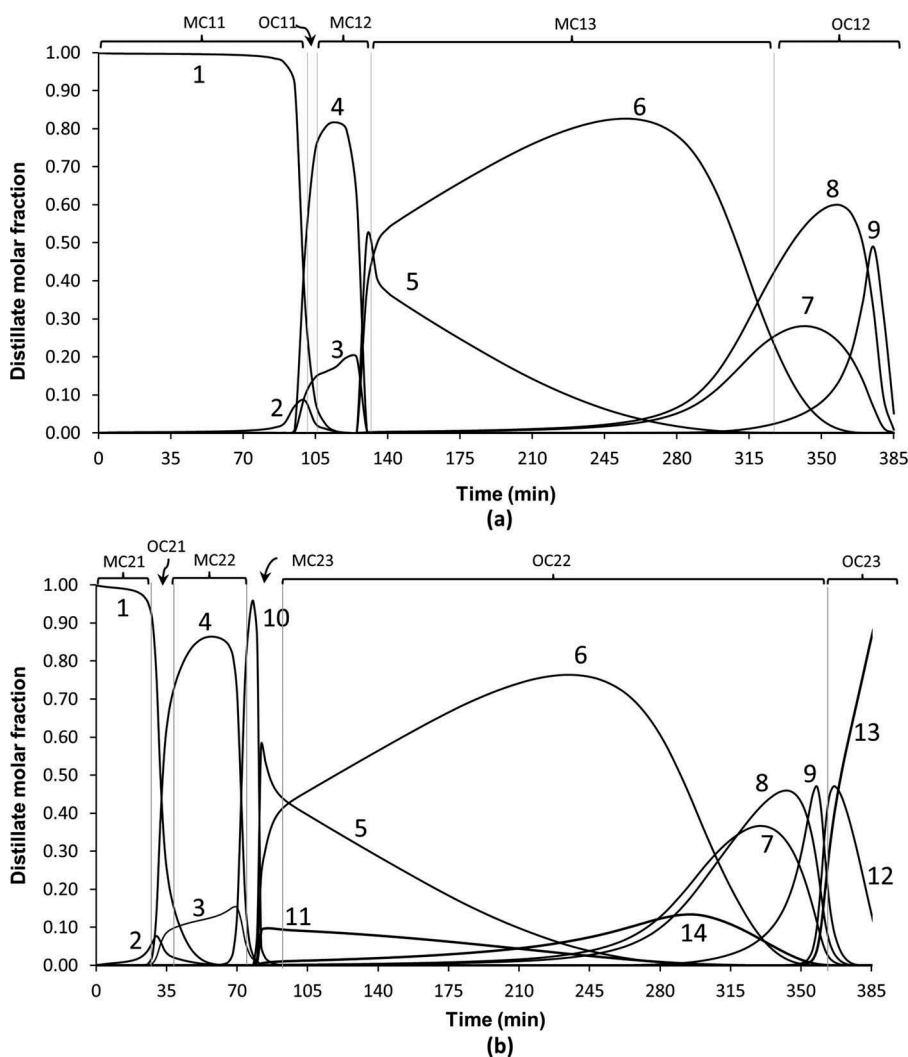
predicting the behavior of essential oil extraction, followed by the definition of the fractional distillation operating conditions to obtain enriched fractions of certain compounds present in the original volatile mixture. The extraction process mathematical modeling was performed following the proposed methodology and the estimated parameters along with their correlation and the determination coefficient for each extraction pressure are presented in Table 5. In Figure 5 are presented the experimental and calculated yield versus time curves of the *A. satureioides* essential oil obtained by steam extraction.

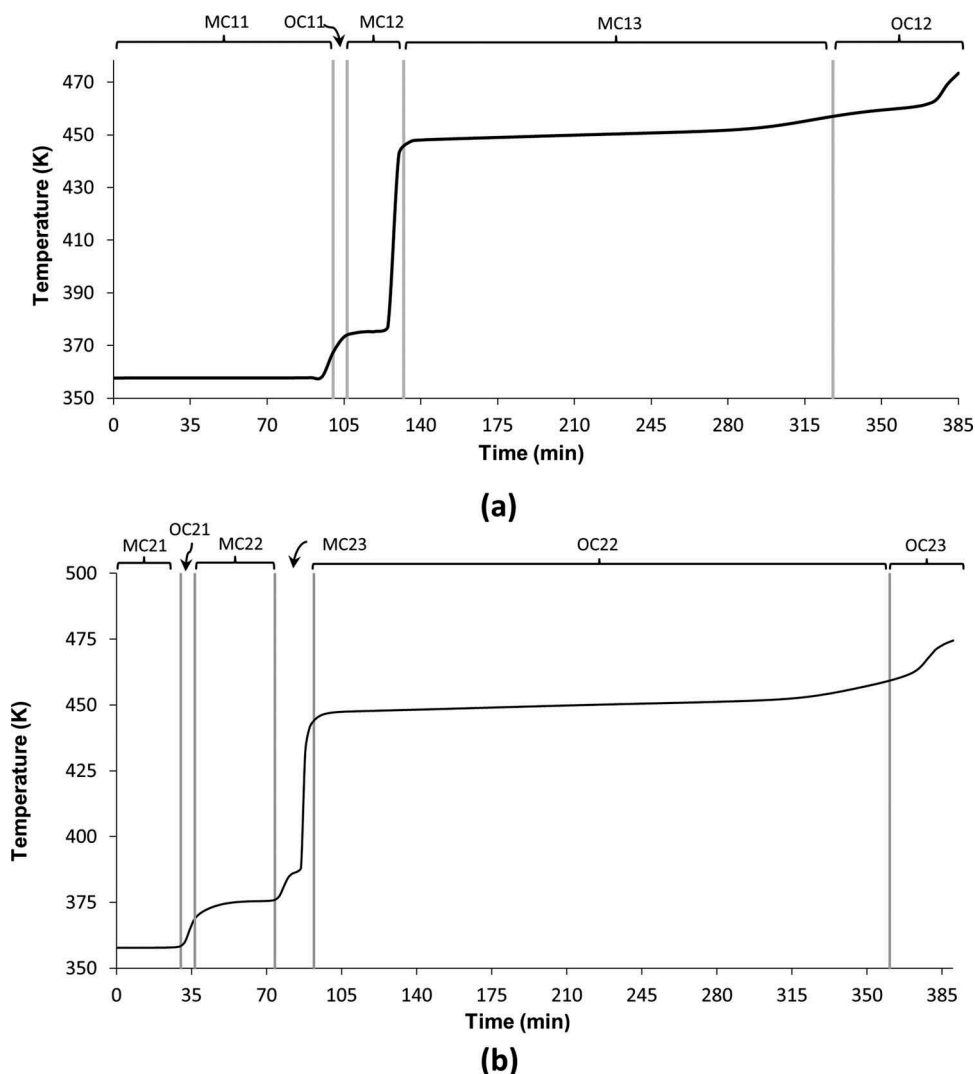
The correlation among the estimated parameters is obtained from the covariance matrix and, as it represents the internal dependence of the estimated parameters, and it is a good criterion, along with the residual sum of squares, in order to obtain the best fitting. The correlation of parameters is directly related to the statistical significance of the estimated value and its confidence interval and if the absolute value of a correlation for a parameter pair is greater than about 0.95, then it may not be possible to estimate the two parameters uniquely using the available regression data (36). The coefficient of determination represents the adhesion of the model to the experimental data.



**Table 4.** Molar fraction of the *A. satureioides* essential oil extracted at 2.5 bar and the main cuts obtained from the simulation of its fractionation process.

	Initial	MC21	OC21	MC22	MC23	OC22	OC23
E-Caryophyllene	0.356	–	–	–	0.001	0.511	–
$\alpha$ -Pinene	0.087	<b>0.987</b>	0.609	0.043	–	–	–
$\alpha$ -Humulene	0.088	0.001	0.290	<b>0.815</b>	0.169	–	–
$\beta$ -Pinene	0.003	0.013	0.058	0.008	–	–	–
(Z) $\beta$ -Ocimene	0.022	–	–	0.012	<b>0.776</b>	0.003	–
$\delta$ -Cadinene	0.069	–	–	–	–	0.096	0.031
$\alpha$ -Copaene	0.103	–	–	–	0.002	0.147	–
Caryophyllene oxide	0.023	–	–	–	–	0.002	0.311
$\gamma$ -Cadinene	0.063	–	–	–	–	0.089	0.011
$\alpha$ -Muurolene	0.024	–	–	–	–	0.027	0.076
Vidiflorene	0.036	–	–	–	–	0.052	–
Aromadendrene	0.030	–	–	–	–	0.043	–
$\beta$ -Selinene	0.021	–	–	–	–	0.031	–
Limonene	0.014	–	0.043	0.123	0.052	–	–
$\alpha$ -Calacorene	0.048	–	–	–	–	–	0.572
Selina-3,7(11)-diene	0.014	–	–	–	–	–	0.002
<b>Recovery<sup>a</sup></b>		<b>7.03%</b>	<b>2.32%</b>	<b>9.61%</b>	<b>2.48%</b>	<b>71.01%</b>	<b>7.20%</b>

<sup>a</sup>Recovery relative to the initial batch load (molar basis).

**Figure 3.** Composition versus time—distillation product of *A. satureioides* essential oils extracted at 1.0 bar (a) and 2.5 bar (b). **1**— $\alpha$ -pinene; **2**— $\beta$ -pinene; **3**—limonene; **4**— $\alpha$ -humulene; **5**— $\alpha$ -copaene; **6**—E-caryophyllene; **7**— $\gamma$ -cadinene; **8**— $\delta$ -cadinene; **9**— $\alpha$ -muurolene; **10**—(Z)- $\beta$ -ocimene; **11**—aromadendrene; **12**—caryophyllene oxide; **13**— $\alpha$ -calacorene; **14**—vidiflorene.



**Figure 4.** Column top temperature profile on the simulated fractionation for the *A. satureioides* essential oils extracted at 1.0 bar (a) and 2.5 bar (b).

**Table 5.** Values of the parameters estimated for the mathematical model used to simulate the steam distillation process for each condition (pressure and interstitial vapor velocity).

Pressure (bar)	$u$ (m/s)	$K$ ( $\text{m}^3/\text{kg}$ ) $\cdot 10^4$	$k_{TM}$ ( $\text{s}^{-1}$ ) $\cdot 10^4$	Correlation	$R^2$
1.0	5.87	$0.972 \pm 0.174$	$7.613 \pm 0.667$	0.8105	0.9884
1.5	4.09	$2.065 \pm 0.366$	$8.152 \pm 0.752$	0.6896	0.9838
2.0	3.17	$5.427 \pm 0.906$	$9.148 \pm 0.910$	0.5581	0.9902
2.5	2.59	$8.810 \pm 1.170$	$8.166 \pm 1.003$	0.5897	0.9875

#### 4 Conclusions

The results generated by the use of different tools to evaluate the pressure effect in the marcela essential oil extraction process by steam distillation: analytical (GC/MS) and statistical (PCA) allow concluding that three essential oil groups are produced with different compositions. The sensorial analysis (GC/O) provided new

olfactometric profiles for the oil of *A. satureioides*, highlighting the smoked and floral odor, identified in the four pressures. Therefore, process pressure influences the essential oil yield, composition and aroma, but this behavior is not proportional to the increase in pressure.

Mathematical model used in this study represented very well the yield versus time experimental curve in the four different pressures, since the estimated parameters  $K$  and  $k_{TM}$  are uncorrelated and the calculated determination coefficients are ( $R^2$ )  $\geq 0.9838$ . It is also concluded that the methodology applied to the *A. satureioides* essential oil batch distillation demonstrated promising potential in the development of essential oil fractionation process in function of the high purity in the  $\alpha$ -pinene fraction and intermediate purity in the  $\alpha$ -humulene E-caryophyllene and fractions obtained.

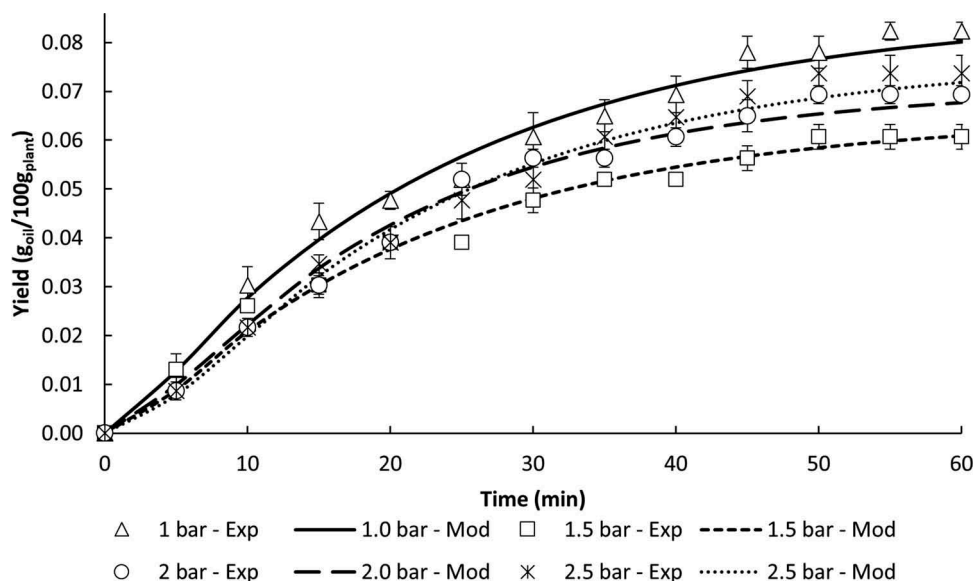


Figure 5. Yield versus time for the experimental and model curves of the essential oil steam distillation from *A. saturoioides*.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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