Optimization of solvent free microwave extraction of natural antioxidant from wood waste

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Abstract
Solvent Free Microwave Extraction (SFME) of oil from maritime pine wood waste and its antioxidant activity were investigated and compared to classical hydrodistillation (HD) method (Clevenger apparatus). A central composite design combined with response surface methodology was applied to evaluate the simultaneous influences of irradiation power, irradiation time and moisture content before SFME. A maximal extraction yield of 0.43% (g/100 g dry wood waste) was achieved under optimal extraction time of 43 min and an irradiation power of 668 W compared 0.28% obtained for the conventional method (HD). The results also showed that the three independent variables had a statistical significant effect on the considered response as well their quadratic effects. Gas chromatography coupled to mass spectrometry (GC-MS) analysis showed that SFME extract is richer in oxygenated compounds (~58.5%) compared to HD extract (34.1%). The comparison of total phenolic compounds (TPC) showed that under optimized condition of SFME procedure, the amount of TPC was 74.6 mg GAE/g extract, largely higher than that obtained for HD extraction (51.2 mg GAE/g extract) suggesting that SFME represents an interesting alternative technology for production of recoverable oil from waste issued from maritime pine wood waste. Moreover, the antioxidant activity assessed by 2,2-diphenyl-1-picrylhdrazyl (DPPH) test showed that the concentration that inhibit 50 of DPPH radical was lower for SFME (15.4 μg/ml) compared to HD (123 μg/ml and to a synthetic antioxidant (BHT) (24μg/ml).

1. Introduction
The lignocellulosic waste materials represent an interesting source of chemicals. Their abundant and renewable origin as well as the qualities found in their components converts them in a promising alternative resource. Maritime pine (*Pinuspinaster*) is a conifer native to South-Western Europe and North-Western Africa, with major forests development on Atlantic coast of southern France, Spain and Portugal [1]. Extracts isolated from plants such as pines are used as fragrances in cosmetics, flavouring 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 [2]. In this field, the traditional synthetic antioxidants food additives such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) showed some negative side effects on health[3] due to their instability and high volatility [4]. Therefore, increasing interest in natural antioxidant present in the diet has developed among consumers and the scientist community an interest to replace synthetic antioxidants [5,6]. A lot of research work have been reported about antioxidant properties of different plant extracts [7,8], and confirmed that the phenolic components in isolated oils were the main source of antioxidant activity [9].The technologies used to extract volatile oils from plant materials are enormous and usually have some disadvantages as high temperature, long processing time as in the conventional hydrodistillation or the solvent extraction in which a loss of volatile compounds occurs during solvent removal [10]. For a few years, the change in attitude has evolved increasingly to a "green" tendency and there has been an increasing demand for new cleaner techniques for essential oil extraction. These new green processes will be more environmentally friendly with a shorter extraction times, lesser consumption of organic solvent and energy, and minor waste and CO_2 emissions, while maintaining a high quality of extract. Some intensified extraction methods were investigated including microwave [11-13]supercritical fluids [14,15], D.I.C-assisted extraction [16,17]or ultrasound assisted extraction [18-20]. Currently, application of microwave technology-based methods such as solvent free microwave extraction (SFME) becomes highly desirable as a valid alternative to conventional methods and this extraction technology was the subject of several studies [21-23]. To the best of our knowledge, no work has been published on the antioxidant activity of oil extracted from industrial wood wastes by solvent free microwave extraction. In the present work, isolation of extracts from maritime pine wood waste issued from timber industry was optimized using SFME method. A central composite design (CCD) has been developed to assess the effect of three independent variables namely microwave irradiation power, irradiation time and moisture content before treatment on extraction yield, on the amount of total phenolic compounds and on the percentage inhibition of DPPH radical (2.2-diphenyl-1-picrylhydrazyl). The results were compared with those of hydrodistillation (HD) as a conventional extraction method.

2. Materials and methods

2.1. Plant material and chemicals

Maritime pine *(Pinuspinaster)* sawdust waste (fig.1) was collected in Southern France after wood sawmilling by Archimbaud company (Secondigné/Belle, France). The form of sawdust was approximately (40 x 3.5 x 0.5 mm). Moisture content was measured using a halogen Moisture Analyzer (Ohaus – MB 35) at 105°C and corresponded to 43 % db (dry basis). After storage in a refrigerated room at 4°C, fresh sawdust waste material was employed in all extractions. 2,2-Diphenyl-1-picrylhydrazyl hydrate (DPPH), anhydrous sodium carbonate, gallic acid, Folin–Ciocalteu's phenol reagent were purchased from Sigma–Aldrich and Methanol, Na_2CO_3 were from Fisher scientific.

2-2. Protocol

In the present study, the experimental design was achieved as illustrated in Fig.1. Extraction of volatile molecules was performed by HD and SFME methods. Each HD operation was performed three times. SFME treatments were analysed and optimised through statistical study. For HD and for SFME in optimised conditions, the antioxidant activity and total phenolic compounds were evaluated.

2.3. SFME apparatus and procedure

Solvent-free microwave extraction has been performed on a Milestone NEOS microwave station (NEOS microwave laboratory oven) (Fig.2). It is a multimode microwave reactor 2.45 GHz with a maximum delivered power of 1000 W variable in 10 W increments. Temperature was monitored by an external infrared sensor. In a typical procedure 100 g of moistened bark chips were subjected to microwave irradiations in oven cavity, initially at ambient temperature, during a fixed processing time. The microwave heating of the water contained inside the raw material allows releasing molecules constituting isolated oil. This oil was then driven by the generated vapor. A cooling system outside the microwave cavity permitted to condensate the distillate continuously (5 °C). Condensed water was refluxed to the extraction vessel in order to provide uniform

conditions of temperature and humidity. Isolated oil was dried with anhydrous sodium sulphate and stored at 4 °C in the dark until used. Extraction yield was calculated according to eq.1

$$\text{Extraction yield } (\%) = \left(\frac{\text{mass of extracted essential oil}}{\text{mass of dry material}} \right) \times 100 \qquad (eq.1)$$
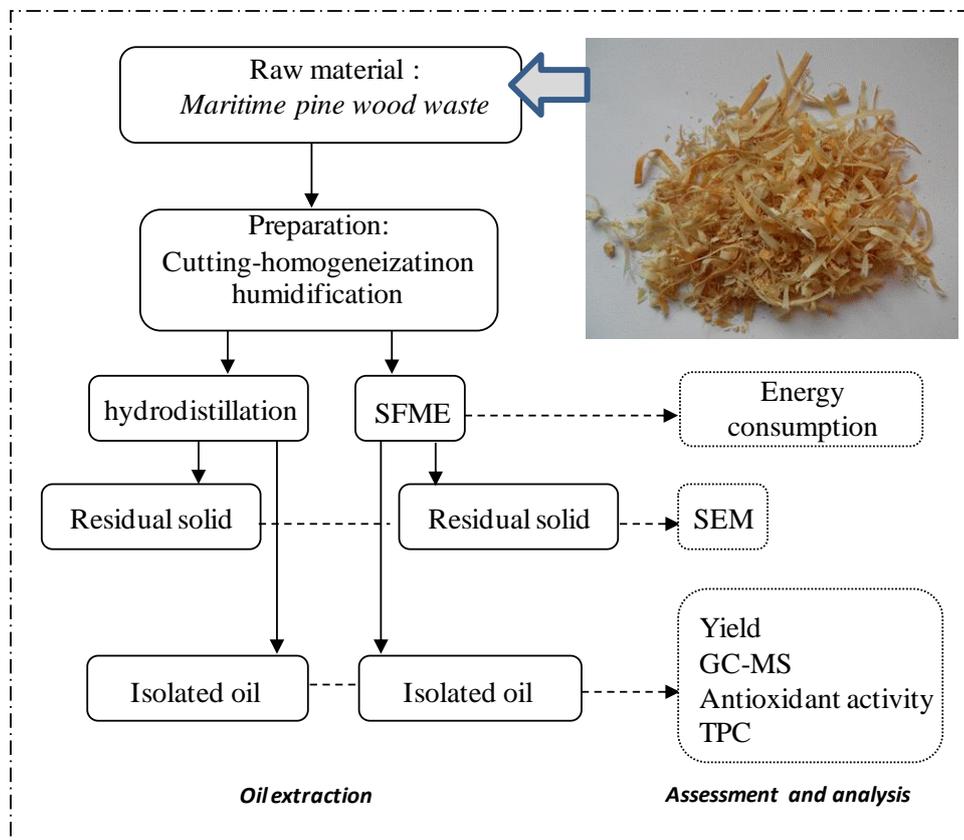

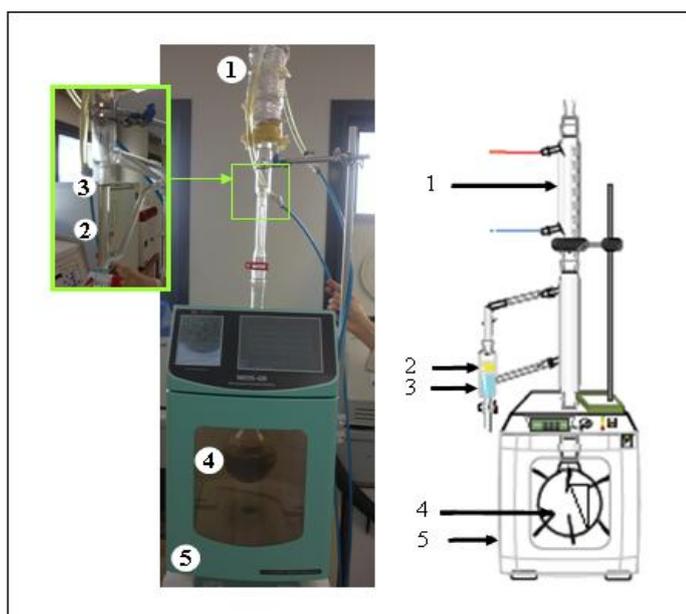**Figure 1.** Protocol of extraction and analysis of oil from maritime pine bark waste.

Figure 2. Solvent free microwave extraction apparatus (SFME): (1) refrigerant system; (2) aqueous fraction; (3) oil fraction; (4) maritime pine wood waste; (5) microwave oven.

2.4. Hydrodistillation apparatus and procedure

Conventional hydrodistillation apparatus (Clevenger-type apparatus) according to the *European Pharmacopeia* [24]was employed. A quantity of 100 g of maritime pine wood waste for 9 L of distilled water was used to perform the hydrodistillation during 480 min from the first drop of distillate fell until the raw material has been completely exhausted. Isolated oil was collected, dried under anhydrous sodium sulphate, and stored at 4°C for further analysis. Each extraction was performed at least three times, and a standard deviation was calculated. The extraction yield was calculated according to eq.1.

2.5. Experimental design

The relationships between response functions and process variables have been established by using a central composite design (CCD) [25]as well as the optimal conditions of the developed process. The independent variables were coded according to eq.2:

$$x_i = \frac{X_i - X_{i0}}{\Delta X_i} \qquad i = 1,2 \qquad \text{(eq.2)}$$

wherex_i and $X_i$are respectively the dimensionless and the actual values of the independent variable i, X_{i0}isthe actual value of the independent variable *i* at the central point, and ΔX_i is the step change of $X_i$corresponding to a unit variation of the dimensionless value. Irradiation power (x_1), processing time (x_2) and moisture content before SFME (x_3) were chosen as independent variables. The selected response was the total yield. For the two variables, the design yielded 19 experiments including eight (2^3) factorial points, six axial points (-α and +α) to form a central composite design and five centre points for replications and estimation of the experimental error and to prove the suitability of the model. Both coded and actual values of the independent variables and their ranges of variations are listed in table 1.

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i \neq j} \beta_{ij} x_i x_j \qquad \text{(eq. 3)}$$

The response Y (isolated oil yield)is related to the coded independent variables according to the second order polynomial expressed in eq. 3, with β_0 the interception coefficient, β_i the linear terms, β_{ii} the quadratic terms, $\beta_{ij}$the interaction terms. Fisher test for analysis of variance (ANOVA) performed on experimental data permitted to estimate the statistical significance of the proposed model. Response surfaces as represented by Fig. 3 were drawn by using the *analysis design* procedure of *Statgraphics Plus for Windows* software (Centurion version).

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

	Coded level				
	−α	-1	0	1	+α
Irradiation power (W)	332	400	500	600	668
Processing time (min)	27	30	35	40	43
Moisture content (%)	166	200	250	300	334

α(axial distance) = $\sqrt[4]{N}$, N is the number of experiments of orthogonal design, i.e of the factorial design. In this case α = 1.68. The three variables were studied in five levels

2.6. GC-MS identification

The volatile compounds were analyzed by gas chromatography coupled to mass spectrometry (GC-MS). Analyses were performed on a GC/MS Varian 3900 chromatograph coupled to a Saturn 2100T mass spectrometer using fused-silica-capillary column. The non-polar column was Elite 5MS (30 m x 0.25 mm x 0.25 µm film thickness). GC–MS spectra were obtained using the following conditions: He (helium) as carrier gas at flow rate of 1 mL /min; split mode1:20; 1 µL as injected volume; 250°C as injection temperature. The oven temperature programme was 60°C for 5 min increasing at 2°C/min towards 250°C and held at 250°C during 10 min. The ionization mode used was electronic impact at 70 eV. Most constituents were identified by comparison of their GC linear retention indices (RI), determined with reference to a homologous series of C5–

C32 n-alkanes. The Identification was confirmed by comparison of the mass spectral with those stored in the MS database (National Institute of Standards and Technology NIST08 and Wiley libraries) and also by comparison with mass spectra from literature data[26]. The percentage composition was calculated from the summation of peak areas of the total oil.

2.7. Assay for total phenolics

Total phenols in maritime pine wood waste extracts was determined using spectrophotometric Folin–Ciocalteu method according to the literature methods [27,28]with some modifications, using gallic acid as standard. Extract solution (0.5 mL) of diluted samples were added into test tubes followed by 2.5 mL of Folin-Ciocalteau reagent (20%, v/v). After 5 min., 2 mL of a solution of 7 % Na_2CO_3 was added. All test tubes with the mixture were caped and shaken for 10 s and put on to incubation in a water bath at 45°C for 5 min. Absorbance was measured after 30 min at 765 nm (Helios Omega UV/VIS Thermo Scientific Merk and Co. Spectrophotometer) against blank sample. The same procedure was repeated for all standard gallic acid solutions (2-200 µg/mL) and a standard curve was obtained with Eq.4 (R^2=0.99):

Absorbance = 0.0109 x Gallic acid (µg/mL) + 0.037   (Eq. 4)

The results were expressed as milligrams of Gallic acid equivalents (GAE) per g extract. The analyses were performed in triplicate and standard deviation was calculated.

2.8. DPPH assay for evaluation of antioxidant activity

The chemical compound 2,2-diphenyl-1-picrylhydrazyl (DPPH) is one of the first free radicals used for studying the structure-activity relationship antioxidant phenolic compounds [29]. In this method, the antioxidant activity of oil extract is evaluated in term of the capacity to scavenging free radicals of DPPH formed, according to a method described by Lue et al. [30]. A solution of 4 mg of the radical DPPH dissolved in 100 mL of methanol was prepared. Then 3 mL of this solution was reacted with 1 mL of oil diluted bark extract (dissolved in methanol). The mixture was incubated in dark for 30 minutes at room temperature. The absorbance was measured at 517 nm with Helios Omega UV/VIS Thermo Scientific Merk and Co. Spectrophotometer. The percentage inhibition activity was calculated by eq.5:

$$I\% = \left(\frac{A_0 - A_t}{A_0} \right) \times 100 \quad \text{(Eq. 5)}$$

Where A_0 is the absorbance of the control sample (without isolated oil) and A_t the absorbance of the extract with DPPH at 30min. All analyses were run in triplicates and averaged. Then the concentration that inhibit 50% of DPPH radical (IC_{50}) was determined.

3. Results and discussion
3.1. Regression coefficients and fitting the models
The complete design matrix together with the values of experimental and predicted yields is given in table 2. A regression analysis was carried out to fit a mathematical model to the experimental data aiming at an optimal region for the studied response. The predicted model can be described by table 3 in term of coded values. The significance of each coefficient was determined using Fisher test (*F-value*) and the probability p (*p-value*) in the same table, 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. For the yield of maritime pine wood wasteisolated oil, it can be seen that the linear terms are strongly significant (*p<0.05*) as well as the quadratic terms indicating that a maximum of yield is reached beyond which a degradation is observed particularly for the processing time. According to Abdelhadi et al. [12], this degradation concerns the oxygenated compounds of the oil during a prolonged processing time or for high microwave intensity. The interaction between irradiation power and processing time was also statistically significant with a confidence level of approximately 93 % indicating an antagonistic effect of the two factors. The quality of the developed model was evaluated based on the correlation coefficient R^2 and on the lack-of fit value. From ANOVA (table 3), it can be seen that R^2 was close to 96 % and *p-value* of lack-of-fit higher than 0.05 (non-significant) suggesting that the predicted model reasonably represent the observed values. Thus the responses were sufficiently explained by the model.

Table 2. Experimental data and obtained responses with the different combinations of irradiation power (x_1), irradiation time (x_2) and initial moisture content (x_3)used in the randomized central composite design.

	Coded variable level			Responses data	
Run	x_1	x_2	x_3	Observed	Predicted
1	-1	-1	-1	0.04	0.028
2	1	-1	-1	0.25	0.225
3	-1	1	-1	0.07	0.044
4	1	1	-1	0.29	0.319
5	-1	-1	1	0.06	0,047
6	1	-1	1	0.14	0.135
7	-1	1	1	0.02	0.031
8	1	1	1	0.24	0.241
9	$-\alpha$	0	0	0.01	0,046
10	$+\alpha$	0	0	0.41	0,391
11	0	$-\alpha$	0	0.01	0,044
12	0	$+\alpha$	0	0.15	0.134
13	0	0	$+\alpha$	0.11	0.124
14	0	0	$-\alpha$	0.05	0.053
15	0	0	0	0.13	0.136
16	0	0	0	0.15	0.136
17	0	0	0	0.13	0.136
18	0	0	0	0.14	0.136
19	0	0	0	0.16	0.136
Mean absolute error for replications					0.014
Maximal yield for HD procedure (%) 0.28					

Table 3. On the left: the regression coefficients of the second-order polynomial equation. On the right: Analysis of variance showing the effect of the three independent variables as linear, quadratic and cross products terms.

coefficients	Regression	Source	DF	Sum of squares	F-ratio	p-value
β_0	0.1358	x_1	1	0.1441	726.87	0.0000[**]
β_1	0.2054	x_2	1	0.0097	49.34	0.0037[**]
β_2	0.0535	x_3	1	0.0062	31.26	0.0145[*]
β_3	-0.0426	x_1x_2	1	0.0028	14.19	0.0785
β_{12}	0.0375	x_1x_3	1	0.0021	10.66	0.1214
β_{13}	-0.0325	x_2x_3	1	0.0001	0.06	0.9001
β_{23}	-0.0025	x_1^2	1	0.0134	67.78	0.0012[**]
β_{11}	0.060	x_2^2	1	0.0042	21.31	0.0362[*]
β_{22}	-0.033	x_3^2	1	0.0042	21.31	0.0362[*]
β_{33}	-0.033	Lack-of-fit	5	0.0077	7.81	0.088
R^2	0.963	Pure error	7	0.0013		

*p-value<0.05 ; **p-value<0.01
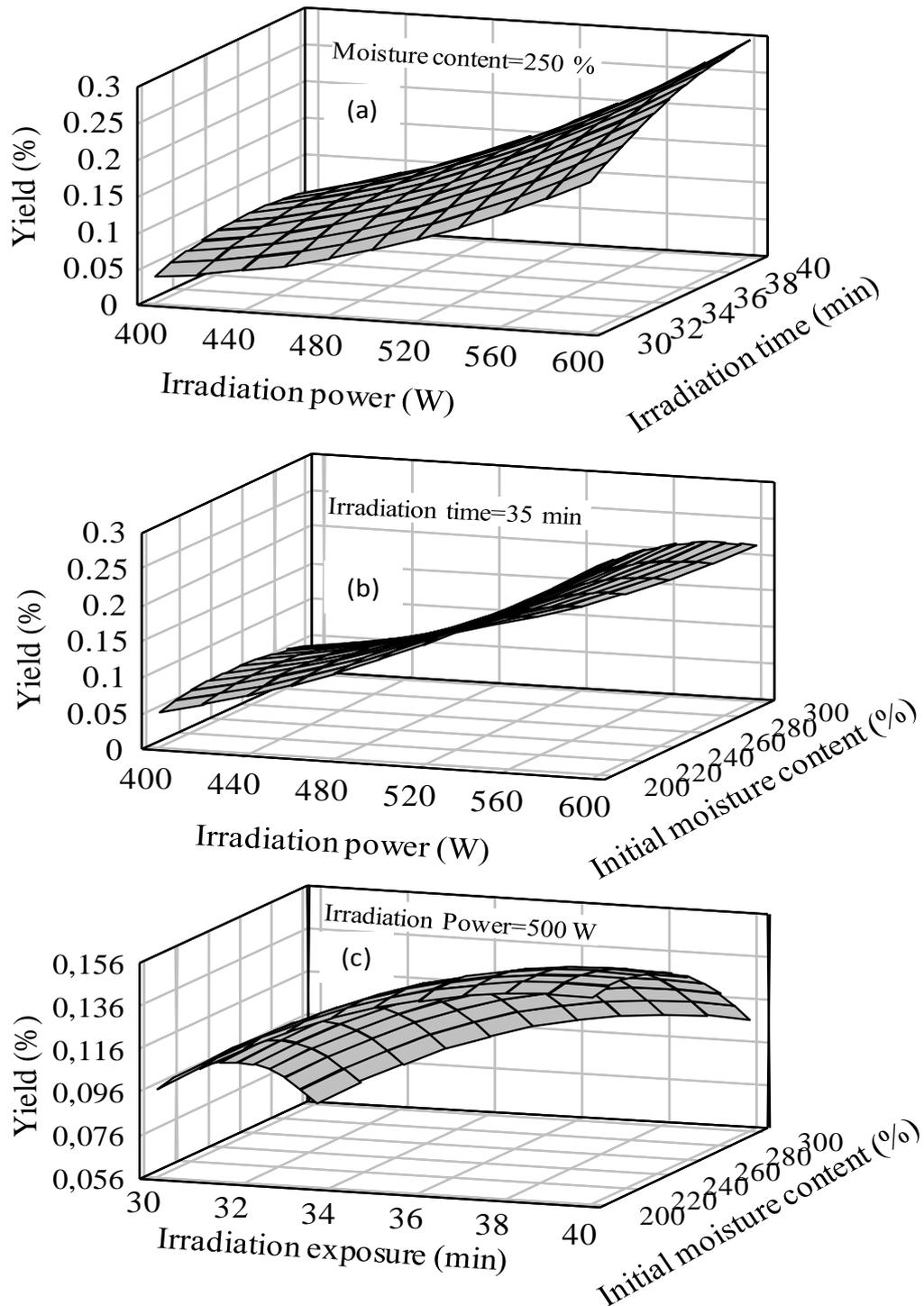
Figure 3. Responses surfaces showing the simultaneous effect of irradiation power, irradiation time and initial moisture content on isolated oil yield.

3.2. Response surface analysis

Three-dimensional profileof multiple non-linear regression model was employed to illustrate the linear and quadratic effects as well as the interaction effects on the yield of extracted oil. Fig.3 highlights the yieldbehavior in function of two variables. In each plot, the third one is fixed at its central value ("0"). The most influential effects on the yield of isolated oil are the linear terms of irradiation power (x_1) and irradiation time (x_2) followed by the quadratic terms of the three studied factors. Fig. 3.a clearly shows that the yield

increased linearly and positively as irradiation power and irradiation time increased. This increasing was also pointed out by Dai and Mumper[31]for which a high temperature favoured the extraction process by enhancing the solubility of phenolic compounds and the mass transfer rate and by weakening the plant tissues. A negative linear effect was exerted by the moisture content. For a fixed irradiation power and irradiation exposure at "0" level, when initial moisture content varied for its low to its high value, the yield decreased from 0.18 % to 0.09 % (fig 3b).At higher water contents, water is stored as free water in the cell lumens. The moisture content, at which the cell walls are saturated with bound water, but the cell lumens (i.e. the voids) inside the wood cells are still empty, is denoted as fiber saturation point (FSP). Below fiber saturation point (FSP), water vapour and bound water exist to significant extent. Beyond FSP, the free water could form a thin layer which prevents the volatiles to leave the matrix [16]. The quadratic effects of irradiation exposure and the initial moisture contents are also clearly visible on figures 3b and 3c. For example, at a fixed central value of irradiation power (500 W) and moisture content (250 %), the yield increased from 0.08 and reached a maximum of 0.15 % beyond which it decreased. Irradiation power also exerted a significant quadratic effect (p=0.012) but it was less predominant as that of irradiation time and as indicated by Fig 4a. and Fig 4b in which the surface curvature is less visible than that of Fig 4c. This quadratic effect may be attributed to the fact that higher concentration of chemical species is present in the cavitation bubbles due to the higher vapor pressure at higher operating temperature which results in much higher amounts of free radicals in the liquid leading to higher degradation rate [8].

3.2. Solvent free microwave extraction (SFME) versus hydrodistillation (HD)
3.2.1. Yield, total phenolics and antioxidant activity

The optimum yield predicted by the model (0.482 %) for irritation power of 668 W, irradiation exposure of 43 min and initial moisture content of 173 %. This result was confirmed experimentally using the optimized operating conditions since the obtained yield was about 0.45 %. Compared to HD the yield was enhanced by about 53 % since the maximal obtained yield was 0.28 %[21]. In the same time, the processing exposure was reduced from 480 min for HD to 43 min for SFME. The most important a difference was observed between the both extraction methods is the ability of SFME process to quickly raise the temperature of the sample to 100 °C. This rapid increasing of extraction temperature gives to acceleration of extraction rates under microwaves and could be due to a synergetic combination of heat and mass transfer phenomena. For HD, mass transfer occurs from inside to outside whilst heat transfer occurs from outside to inside. For microwave extraction, the two transport phenomena act in the same direction, from inside to outside, which facilitates oil diffusion [32, 33].

Table 4: Comparison of extraction yield, TPC amount and the percentage of DPPH inhibition for SFME (43 min, 668W) and HD (180 min).

	Yield (g/100 g d.b)	TPC (mg GAE / g extract)	Inhibition (μg/ml) IC_{50}
SFME		74.62±1.7	15.4±1
HD		54.14±1.5	123.0±5.4
BHT			24.0±0.4

The Folin-Ciocalteu method allowed a good discrimination between the SFME and HD extracts (Table 4). The results clearly shown that the application of microwaves leads to recover phenolic compounds with a higher concentration in comparison with hdrodistillation, respectively 74.62 and 54.14 mg GAE/g extract for SFME and HD.The same result was pointed out byPérino-Issartier et al.[34] who compared SFME and conventional extraction process for extraction of antioxidant from sea buckthorn. According to these authors, the influence of microwave energy on extraction is strictly thermal and the displayed energies (1.24×10^{-6} eV - 1.24×10^{-3} eV) are much lower than that of usual ionisation energies of biological compounds (13.6 eV), covalent bond energies as OH (5 eV) or hydrogen bond (2 eV).

To assess the antioxidant activity, we used DPPH radical method.A freshly DPPH prepared solution gave a deep purple color which generally fades when an antioxidant is present in the medium. This transformation is

spectrophotometrically measured and the disappearance of the purple color monitored at 517 nm.All extracts exhibited concentration-dependant DPPH radical scavenging activity.

The extracts isolated by the conventional method (HD) revealed moderate antioxidant activities as indicated by the values of IC_{50} in table 4 in which are displayed the $IC_{50}$for SFME and HD methods as well as that of the reference compound BHT (Butylhydroxytoluene) which is known as a very efficient synthetic antioxidant agent and widely used in food technology. It appears that SFME extract showed the lowest IC_{50},indicating that it was the most effective against DPPH radical even compared to BHT synthetic antioxidant. It is then obvious that microwave extracts could effectively replace the synthetic antioxidants due to their promising radical scavenging activity. On other hand, a positive correlations between the IC_{50} percentage inhibition of DPPH and total phenol content was explored for the extracts obtained by the two extraction methods. The relatively high regression coefficients R^2 (0.95-0.98, $p<0.01$) indicates that the total phenols are highly contributes to the antioxydant activity.

3.2.2. Chemical composition
For both HD and SFME isolated oils, about 44 components were respectively identified among which monoterpene and sesquiterpene hydrocarbons as well as oxygenated monoterpenes andsesquiterpenes[18].From table 5, it can be seen that for SFME isolated oil the predominant group is that of oxygenated compounds (58.5 %) compared to HD (34.1 %). Orio et al. [35]connect this phenomenon to microwave energy effect which differs for oxygenated and non-oxygenated groups of compounds. For the more polar compounds (oxygenated), the more easily the microwaves irradiations are absorbed, the better the interaction between electromagnetic wave and matter is established and more polar aromatic components are obtained, conversely to sesquiterpenes and monoterpenes hydrocarbons. Electromagnetic interactions are also cited as possible cause to presence of more oxygenated compounds in SFME extracts: organic compounds that have a high dipolar moment as many oxygenated compounds interact more vigorously with microwaves and can be extracted more easily. It should be noted that the oxygenated compounds are most valuable in plant isolated oils; they are characteristic of a strong odor and are known to play a key role in the antioxidant activity. Among the oxygenated compounds, terpin-4-ol seems to be predominant in SFME extracts (10.1 %) and probably have also a part in antioxidant activity as it was remarked by Li et al. [36].

Table 5: Percentages of classes of compounds identified in volatile oil isolated from maritime pine wood waste

Group of compounds	HD (%)	SFME (%)
Monoterpenes hydrocarbons	12.4	1.3
Oxygenated monoterpenes	3.5	18.9
Sequiterpenes hydrocarbons	53.5	40
Oxygenated sequiterpenes	15.8	6.4
Other oxygenated compounds	14.1	32.8
Total oxygenated compounds	34.1	58.5
Total non oxygenated compounds	65.2	41.3
Total identified compounds	99.3	99.8

3.2.2. Energy consumption and environmental impact
The reduced cost of oil extraction is clearly advantageous for SFME method in terms of energy and time saving. HD method required 480 minutes to reach a maximum yield of 0.28% while 43 min. were sufficient to reach a maximum yield 0.43% for SFME.The amounts of water to evaporate were 9 kg for HD and about 98 g for SFME. Then, the energy required for performing HD and SFME extraction methods were respectively 8 kWh and 0.55 kWh (in optimised conditions).Regarding the environmental impact, the calculated quantity of carbon dioxide rejected in the atmosphere for HD was from 5984 g to 8000 g CO_2, largely higher than that of SFME (from 411 g to 550 g CO_2). These calculations were preformed according to literature provided by the French Nuclear Energy Society (http://www.sfen.org/fr/lenergie-nucleaire/nucleaire-et-environnement; downloaded on June 25, 2015): to obtain 1 kWh from coal and fuel, respectively 1000 g and 748 g of CO_2 is rejected in atmosphere during combustion.

Conclusion

This study focused on the optimization of SFME extraction process for isolation of oil from wastes of maritime pine wood. The maximum extraction yield was obtained for 668 Was irradiation power, 173 % as initial moisture content and 43 min as processing time was 0.43%, higher for that obtained with a conventional method (HD) for which the maximum extraction yield was 0.28 % obtained for 8h processing time. Moreover, the oil extracted under microwave irradiation was found to possess an improved antioxidant activity combined with a high quantity of phenolic compounds compared to HD method. Thus we can conclude that SFME is a green extraction method that offers important advantages as short extraction time, low energy input and no requirement of solvent. Thus the sustainability of the wood processing industry can be improved through the use of by-products, by adoption of new technologies that maximize process profitability

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(2017) ; http://www.jmaterenvironsci.com