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Phytosanitary Decontamination of Crude Rapeseed Oil by Instant Multi-Flash Autovaporization (MFA)

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Abstract: Despite their well-known harmfulness to human health, pesticides persist largely used for plant cultivation. These molecules are highly resistant to degradation by plant metabolism, while their presence, even as traces is dangerous at phytosanitary quality and environment impact. Now, due to regulations and quality standards, food industries seek to control these contamination risks and conduct research on technologies able to efficiently eliminate pesticide residue traces. Since the mechanisms of eradicating molecules are classified in three ways of evaporation, dissolution, and thermal degradation; the decontamination process should depend on three important factors: i/ the nature of the products (composition and technological/structural aptitude), ii/ the nature of the pesticides (volatility, solubility, and thermal stability), and iii/ the type of the disinfection process. The instant treatment operations have the particularity of 1/ weak thermal degradation because of HTST (high-temperature/short-time) nature; 2/ frail solubilizing by using the steam instead of liquid soaking as heating fluid, and 3/ favorable elimination of vapor molecules through the instant autovaporization. Therefore, the present study aims at the application of the multi-flash autovaporization MFA technology in the treatment of tetrachloro-m-xylene, aldrin, γ-chlordane and dieldrin pesticide residues in the case of rapeseed oil (brute). This resulted in drop-down levels of 45.2%; 30.6%; 32.2%; and 29.2%, respectively for the initial concentrations of 5, 4.51, 1.98 and 3.98 (10^{-2} mg/kg of oil), respectively. Far from a real optimization of the operation, 51-cycle MFA at a heating temperature of 50 °C reduced the total pesticide concentration from 15.39 to 9.99 (10^{-2} mg/kg oil) .

Keywords: Multi-Flash Autovaporization (MFA); Rapeseed Oil; Organochlorine Pesticides; Fatty Acids; Tocopherols; Statistical modeling.

Abbreviations: C: Number of cycles, **T:** Temperature (°C)**, t**: Time (min), **RM:** Raw Material, **GC:**Gas chromatography, **GC-MS:** Gas chromatography coupled with mass spectrometer**, HPLC:** High-Performance Liquid Chromatography, **CPA:** Central Point Average, **P:**Absolute pressure (Pa), $\mathbf{P_{int}}$**:** Absolute initial pressure (Pa), $\mathbf{P_{fin}}$**:** Absolute final pressure (Pa), **s:**second, **α:** Atmosphere Reduction Ratio (%), **DRR:** Decontamination Reduction Ratio.

Practical applications

In the field of edible oil industry, all the research work carried out is generally aimed at improving the extraction and refining procedure to ensure higher yields with preservation or improvement of oil quality. Nevertheless, the phytosanitary quality (pesticides) of rapeseed oil has become a critical issue on an industrial scale because of the pesticide residues toxicity as well as the oil sensitivity to the process of degradation or decontamination. Based on the theory of evaporation and volatility using the new design or technology of Multi-Flash Autovaporization (MFA), the main objective is the efficiency study of a high-temperature / short treatment -time (MFA) at the level of decontamination process eliminating the traces of organochlorine pesticides.

INTRODUCTION

Vegetables play a particularly important key role in healthy eating because of the nutrients and minerals they contain. However, at the same time, agricultural procedures can also make them a source of pernicious toxic substances as pesticides [1]. Indeed, the conventional strategy of agricultural techniques involves the use of pesticides as plant protection molecules acting against pests, insects, diseases and weeds and regulating their growth. Dauguet and Lacoste confirm the presence in oilseeds levels that can easily reach 0.1 to 0.25 mg of various types of pesticides/kg, or possibly 1 mg/kg [3, 2].

Numerous study works have proved that such a contamination may exceed the internationally recommended standards especially in the case of oleaginous. Furthermore, in the case of oil extraction by organic solvent (n-hexane), the contamination level increases and becomes more frequent and more significant by combining pesticides with solvent, in both crude oil and meal, because the lipophilic nature of numerous pesticides greatly favor their entrainment with the solvent during the extraction operation [3].

The use of pesticides for growing oilseeds is generally regulated by rules of good practice. However, despite this, various analytical studies have clearly shown that crude vegetable oils may contain too high residual levels of different pesticides. Classic refining methods seem unsuitable or unable for dealing with situation [4].

Therefore, developing profitable and adequate treating procedures to eliminate pesticides is crucial. Some conventional procedures using physical, chemical or biological operations were ineffective for mineralizing or eliminating the pesticides and allowed only their removal to another phase which involves supplementary separation procedures that increases operational costs [5, 6]. The aim of this research was to study the effectiveness of multi-flash autovaporization MFA technology in phytosanitary decontamination by eliminating organochlorine pesticides.

In the current research work, four pesticides were studied: dichlorvos, malathion, pirimiphos-methyl, and fenitrothion [7]. Their behavior greatly depends on their own physicochemical properties and thermal stability. The conventional way of steam flow deodorization is a high temperature treatment as a key factor to guarantee an effective rejection of these pesticides [8]. For a higher level of pesticide residues, different refining steps must be managed, including a specific strong use of a high temperature deodorization and a large amount of scrubbing steam.

Heat treatments such as drying, pasteurization, sterilization, and bleaching are among the most applied processes in the thermal treatment of food products for guaranteeing quality preservation throughout the production chain [9]. All these treatments would degrade or neutralize macromolecules however without completely removing all such traces of pesticides [10]. They also may result in inducing some quality degradation of these foodstuffs [11] Heating of a food product unavoidably results in increasing pressure of vapors of water and other volatile compounds; hence the phenomenon of co-distillation would be able to decontaminate the foodstuffs by denaturing or evaporating pesticide molecules [12].

Hence, since food processing is a succession of techniques and unit operations that act differently on the raw material to obtain a finished product with well-defined physicochemical properties, the sensitivity of pesticides versus extraction and refining techniques depends on their physical and chemical properties (hydrophilic/hydrophobic…) [13].

For example, Miyahara et Saito proved that the soybean oil concentration in dichlorvos and marathon considerably decreases after each Alkali-refining operation [14].

A succession of operations of solvent extraction and refining processes of soybean oil shows a highly significant decrease in pesticide concentration up to 70 % reduction [15], and previous studies show that deodorization processes at temperatures of 240-260 °C remove most pesticides [16, 8].

MATERIALS AND METHODS

Raw materials and Chemicals; Analytic Standards

Crude and degummed rapeseed oil (variety Pioneer 72) from Tunisian production was supplied from the Tunisian company “Carthage Grains (Tunis)”. After assessing their concentrations of fatty acid profiles and different fractions of tocopherols, the main pesticides including organochlorines were identified and measured. Then, the oil was kept at room temperature (about 20 °C) for treatments.

Analytical standards of 22 pesticides residues at initial concentration of 200 µg/ml (Figure-1) provided under the reference Mixed 8081 from Sigma Aldrich. All chemicals (solvents such as hexane, chloroform, Acetonitrile, methanol, acetone…), as well as the standards of α, β, and γ-Tocopherols were supplied by UniLasalle-France. Acetone as solvent was used to prepare a stock solution of α, β, and γ-tocopherol with concentrations of 0.288, 0.656, and 0.348 µg/ml, respectively. The solution was stored at -40°C.

EXPERIMENTAL METHODOLOGY

Generally, disinfection techniques of phytosanitary are classified according to three mechanisms: a/ thermal degradation of the pesticides, b/ solubilizing of the pesticides within water/solvent, and/or c/ co-distillation based on evaporating and removing the vapor of the concerned pesticides.

In order to preserve the quality of processed food product and the thermosensitive compounds it contains, our research work was initiated on the use of autovaporization.

A specific process of multi-flash autovaporization MFA was studied at low temperature and short duration of each cycle of the treatment. Although these conditions weren’t severe and shouldn’t imply any thermal degradation, this work aimed to

study the possible elimination of pesticides by similar co-distillation process.

Figure-1 presents our applied investigation protocol. It began by a fundamental thermodynamic study of the autovaporization phenomenon and the volatility of the main pesticides. These theoretical measurements allowed defining the ranges of MFA processing parameters as the independent operating variables and expressing a relevant basis to well-express an adequate Design of Experiments DoE. Following the preparation and purification of the solutions, a chromatographic assay by GC-MS aimed to determine the concentrations of traces of pesticides (in ppm). The final product quality was recognized through the determination of profiles and concentrations of fatty acids and tocopherol fractions by both GC and HPLC.

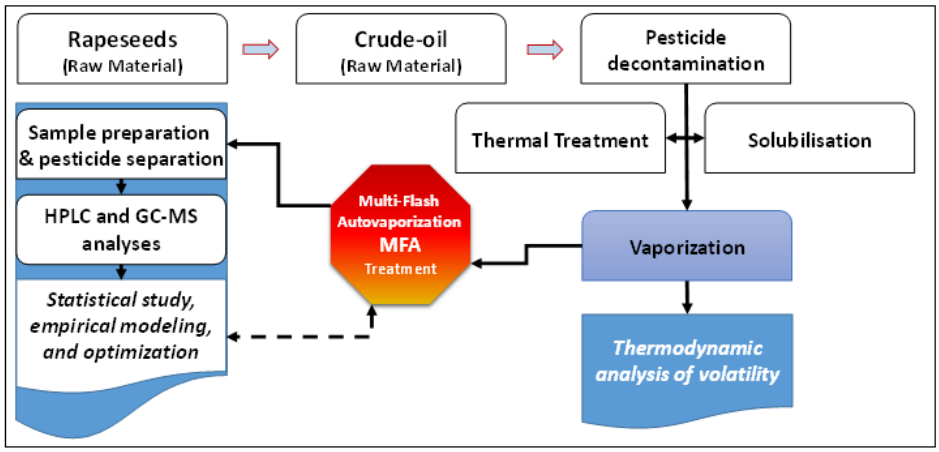

Fig-1: Experimental protocol of rapeseeds oil decontamination by Multi-flash autovaporization MFA

Treatment of crude oil by multi-flash autovaporization MFA

Principe

Based on the phenomena of instantaneous autovaporization due to an abrupt pressure-drop, the operation of multi-flash autovaporization MFA differs from Instant Controlled Pressure-Drop DIC by the fact that it is applied at much lower temperature as an evaporation process which often greatly acts on even weakly volatile molecules.

Technically, MFA is used for thermosensitive products which can undertake even at low temperature treatments (ambient-100 °C). MFA allows the product to undergo a succession of compression/pressure-drop cycles using the compressed dry air instead of saturated dry steam, which is used in the case of the DIC. In both cases, for each cycle, the short-time compression stage is followed by an instantaneous release towards a lower pressure (5 kPa).

During each cycle, a part of the volatile molecules will be removed by autovaporization and the quantity evaporated depends on 1/ the physicochemical properties (volatility) of the molecules themselves, 2/ the surface of exchange product/compressed gas, 3/ the structure of product, and, also 4/ the processing conditions (atmosphere pressure and temperature, ...). In the present case of pesticide decontamination, MFA autovaporization was performed using compressed air at room temperature.

Experimental set up

The MFA technology shown in Figure-2 Consists in subjecting the sample to a cyclic pressure variation after placing it in a hermetic chamber (1). Each treatment cycle is composed of two phases one of compression up to 1 MPa (2), which is controlled by an air intake valve (3) and an abruptly-opening pneumatic valve (4) providing an instantaneous decompression phase ($dP/dt>5$ MPa s^{-1}) by connecting both treatment chamber and vacuum tank (5). The closing of this valve marks the end of a cycle and the beginning of the next cycle.

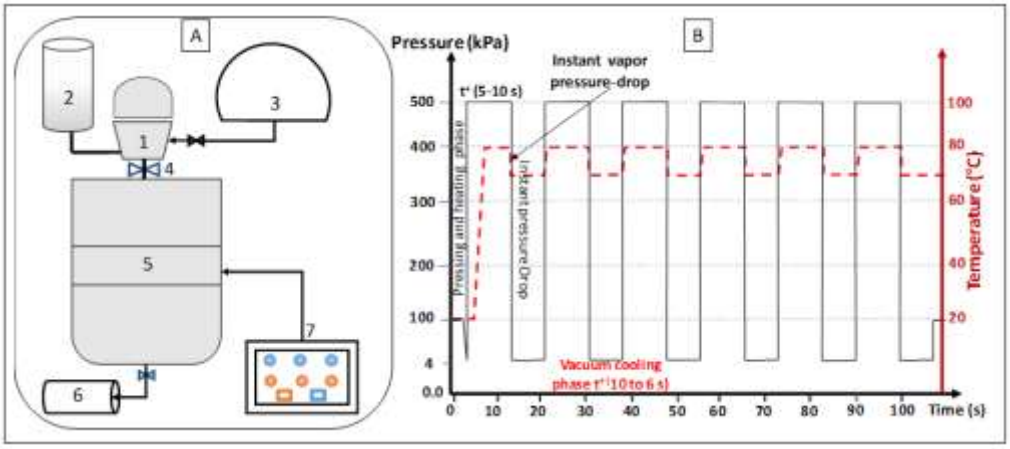

Fig-2: (A and B) Schematic diagram of multi-flash autovaporization MFA system: 1/ Treatment vessel; 2/ Compressed air-heating source; 3/ Water-ring vacuum pump; 4/ Large section-instant opening valve; 5/ Vacuum tank; 6/ Generator of compressed air; 7/ Control and command board.

The profile of the pressure described in Figure-2**Error! Reference source not found.** shows that the pressure measured at the treatment chamber level varies between a high-pressure level rated P^+ and a low-pressure level rated P^-. The first cycle starts by establishing an initial vacuum stage followed by the several following steps:

- 1/ a high air-pressure of 316 kPa. Independently, the product may be heated by various ways of hot air and/or Infra-Red IR, usually up to 100 °C, for a time period noted t^+ of about 10 s. The temperature level of the surface of the product should define the vapor pressure values p_i^+ of each of the different volatile compounds.
- 2/ an instantaneous decompression phase towards a vacuum pocket pressure (5 kPa). This passage reduces by the ratio of molecules removed of each vapor compound:

$$\alpha = \frac{p_i^+ - p_i^-}{p_i^+} = \frac{P^+ - P^-}{P^+} \approx \frac{316\ kPa - 5\ kPa}{316\ kPa} \approx 98\% \qquad Eq.\ 1$$

This reveals that in the present case, at each pressure drop, 98% of the concentration of volatile molecules in the "atmosphere are rejected and eliminated. Since the decompression is instantaneous and due to the presence of a vacuum, the amount of heat exchanged on the surface of the product is low, even during the entire tempering time noted t^- usually of 10 s. Thus, just after decompression, the oil surface temperature doesn't change and was maintained at the initial value. Hence, the oil surface instantly releases the same amount of vapors present just before the pressure drops. Due to this instant autovaporization process, the product cools and a certain quantity of volatile molecules is captured by the relatively cooler surface.

At this time, the next cycle occurs and by injecting the airstream of the next cycle, the heating of the product surface occurs. Cycle after cycle, a probably relevant elimination of volatile compounds takes place. This is the basis of the new deodorization process of Multi-Flash Autovaporization MFA.

Assessments and quality measurements
Extraction and analysis of organochlorine pesticides
Sample preparation and extraction procedure

The separation method used a Maxi-clean™ 900 mg Amino column, with methanol, solutions of (2:1) chloroform/isopropanol and (98:2) diethyl ether/acetic acid solutions. The column was first activated by twice injecting 2 ml of hexane and then 100-120 µl of oil into the column with 20 µ of an internal p-terphenyl standard.

Step.1./A first phase of activation of the column was carried out by twofold injecting 4 ml of hexane. Step.2/ An injection of 100 µg of degummed rapeseed oil + 20µl of a p-terphenyl internal standard solution was followed by injecting 8 ml of a chloroform/isopropanol solution (2:1) to have the fraction F1. Step.3/ An injection of 4 ml of a diethyl ether/acetic acid solution (98:2) gave the fraction F2. Step.4/ An injection of 4 ml of methanol (100%) was performed to recover the fraction F3. Step.5/ The evaporation of the three fractions F1, F2, and F3 under Sorbonne was achieved with compressed nitrogen at a temperature of 50°C. Step.6/ In a new conditioned column (activated), 200 µl of the purified F1 fraction (after evaporation of the solvents) with 4 ml of a 100 % hexane solution were injected to recover the F4 fraction. Finally, the Step.7/ The purification of the

fraction F4 which contains the internal standard, and mixed standard was operated under Sorbonne.

GC-MS conditions

The GC-MS analysis was performed by a GC model Agilent 7890A using an automatic injector 7693. The mass detector MS (model Agilent technologies polo; CA, USA) had an identification and quantification software of type Masse-hunter B0700 Agilent. At a set injection, a separation temperature of 280 °C took place on a HP-5MS column (30 x 0.25mm, 0.25 pm thick).

The carrier gas was helium with a flow rate of 1ml/min with a sample volume set at 1µl. The temperature variation throughout the separation was programmed to rise from 60 to 120 °C with a rate of 40 °C/min, to reach 280 °C (5 °C/min) and remain stable at this level for 30 min. The total separation time was 45 min per injection.

The identification of the pesticide spikes obtained was determined on the basis of retention time. This was followed by integrating all the spikes plus an injection of a mixed standard concentration range (**ref: 8081**) to determine the concentration of the already identified pesticides.

Gas chromatography conditions

The different fractions of the free fatty acids were dosed by an Agile Gas Chromatography 19091S-433 (Kyoto, Japan) equipped with a column (HP-5MS 30 m*350 µm*0.25 µm). The oven temperature was set to increase from 155 to 230 °C with a progression of 45 °C/min.

The final phase temperature was stabilized at 240 °C for 50 min. The mobile phase or the carrying gas was helium sent at a speed of 37 cm/s. We prepared 15 µl of oil samples in a vial + 20 µl TMH+1 ml of methanol-chloroform solution (50/50). A 1 µl injection of each sample was set up automatically in split mode (1/200). The identification and the concentration rates of fatty acids were determined based on an integration of the peaks and the internal program library.

Liquids chromatography analysis

Liquid chromatography quantification used i/ a shimadzu system equipped with two distribution pumps (LC-10AD) and a FL/FR-10AXL detector, ii/ an automatic injector (25µl/samples), and iii/ Altimma RPC-18 separation column (250x4.6 mm. 5µm Associates Inc.).

The mobile phase was an acetonitrile/methanol solution (75:25) injected at a flow rate of 1 ml/mm. The column temperature was stabilized at 250 °C and the fluorescence detector was set at 298 nm for excitation and 344 nm for emission wave. Total separation time was 40 min. The identification and determination of the concentration of the different tocopherol fractions were based on the retention times with the calibration range of the standards α, β, and γ.

Design of Experiments DoE

The principle of experimental designs is to perfectly identify the independent experimental parameters, as well as their ranges in order to best describe the operation. The use of this methodology allows the maximum response to be obtained from a reduced number of tests. To study the effects of the three MFA parameters: heating temperature (T) and treatment time defined by the number of cycles (C) on the concentration of the four (organochlorine) pesticides in crude rapeseed oil (response), a composite central plan with two variables was adopted using the response surface methodology (RMS).

The empirical polynomial regression methodology is used to optimize the applied parameters (factors), based on the analysis of the variance of the experimental results (ANOVA). This allows the identification of significant differences between the independent variables (heating temperature T and number of cycles C). The Independent variables had a statistical significance of 5% probability level ($p< 0.05$) were revealed through Pareto charts. Then to build response surface, the software used a quadratic model equation.

Table-1: Independent variables (factors) and levels used in the treatment experimental process.

MFA parameters:	Temperature T (°C)	Number of cycles (C)
Coded values	Real values	Real values
-α	20	200
-1	29	539
0	50	1350
1	71	2163
+α	80	2500

RESULTS AND DISCUSSION

Determination and identification of pesticides residues

The GC-MS chromatographic analysis allowed detecting, identifying, and measuring the four major pesticide spikes based on retention time; by injecting a mixed standard (22 pesticides, ref:8081).

The detection of Tetrachloro-m-xylene ($C_8H_6Cl_4$.243/ 94 g-mol^{-1}), Aldrin ($C_{12}H_8Cl_6$/ 364.90 g-mol^{-1}), γ-chlordane ($C_{10}H_6Cl_8$/ 409.78 g-mol^{-1}), Dieldrin ($C_{12}H_8Cl_6O$/ 380.91 g-mol^{-1}), and P-Terphenyl was used as the internal standards (Figure-3 & 4).

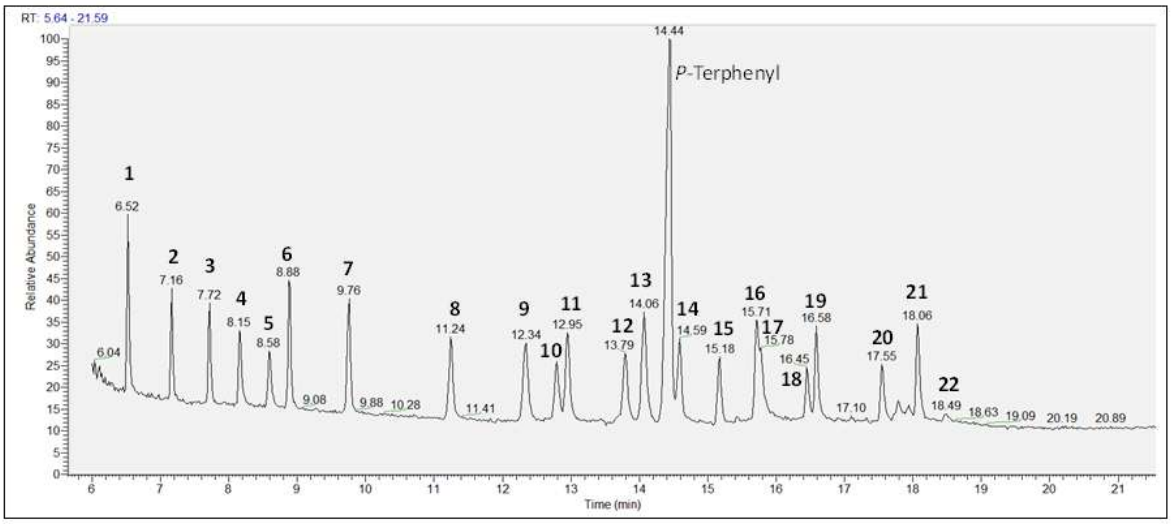

Fig-3: Chromatogram of the pesticide standard mixture at 100 µg.mL^{-1}.(1) Tetrachloro-m-xylène. (2) α-BHC. (3) β-BHC. (4) γ-BHC (Lindane). (5) δ-BHC. (6) Heptachlore. (7) Aldrin. (8) Heptachlore epoxide. (9) γ-Chlordane. (10) Endosulfane. (11) α-Chlordane. (12) 4.4-DDE. (13) Dieldrin. (14) Endrin. (15) 4.4-DDD. (16) Endosulfan. (17) Endrin aldehyde. (18) 4.4-DDT. (19) Endosulfan sulfate. (20) Methoxychlore. (21) Endrin ketone. (22) Decachlorobiphenyl.

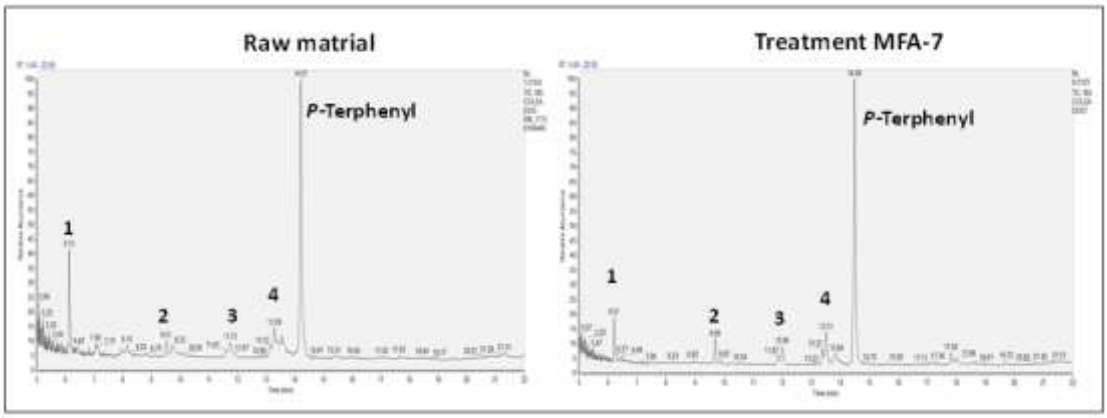

Fig-4: Mass chromatograms of organochlorine pesticides in the degummed rapeseed oil: (1) Tetrachloro-m-xylène; (2) Aldrin; (3) γ-chlordane; (4) Dieldrin; and the intern-standard (P-Terphenyl) after the treatments MFA-7.

Study of pesticides volatility

The different identified pesticide molecules were studied in terms of thermal properties and absolute volatility to recognize the possible decontamination source versus the autovaporization technology.

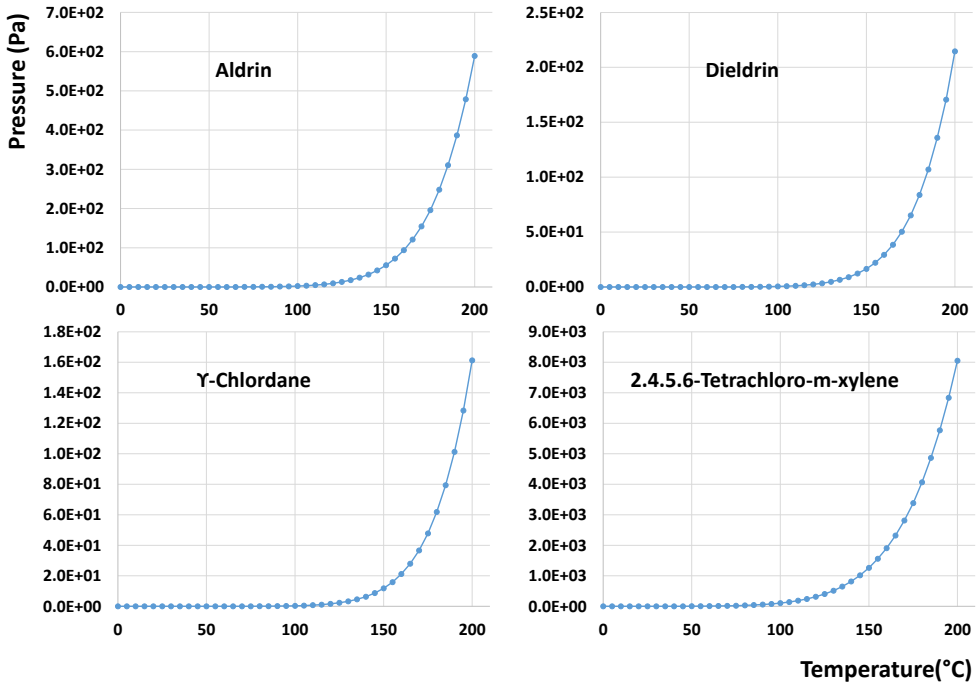

Fig-5: Vapor pressures versus temperature

The measurement of the absolute volatility (vapor pressure) expressed in Pascale (Pa) of the different pesticides as a function of temperature (°C) was illustrated in Table-5.

Pesticide decontamination of rapeseed oil by multi-flash autovaporization MFA

The Table-2 represents the variation in pesticide concentration (mg/kg oil) versus the operating parameters temperature T (°C) and the number of cycles C of MFA treatment. The concentration of pesticides determined by chromatographic assay (GC-MS) is expressed in (mg pesticide/kg crude oil).

RSM modeling and optimization of decontamination of organochlorine pesticides of crude rapeseed oil

Statistical (stratigraphic) studies based on analysis of variance (ANOVA) (Table-2). Pareto diagrams, estimated response area and standardized effects (Figure-6 A, B, C, and D) whose independent variables are heating temperature(°C) and number of MFA cycle applied for decontamination of each pesticide (mg/kg) with (P_{value}=0.05).

The results in Table-2 and Figure-2 confirm the highly significant effect of the variation in the two operating parameters, MFA temperature and number of cycles of treatments on the reduction in the concentration of the four pesticides detected. The optimum conditions reached 45.2%, 30.6%, 32.2%, and 29.2% for Tetrachloro-m-xylene, Aldrin, γ-chlordane, and Dieldrin, respectively.

Table 2. Multi-flash autovaporization MFA decontamination: Impact of parameters on pesticide concentration

		RM	CPA	MFA2	MFA3	MFA5	MFA6	MFA8	MFA9	MFA11	MFA12
Pesticides	MFA cycles C	-	1350	1350	2500	2163	537	537	2163	1350	200
	MFA T (°C)	-	50	80	50	71	71	29	29	20	50
Tetrachloro	Pesticides (mg/kg) /MFA treatment	0.05	0.03	0.03	0.03	0.03	0.04	0.04	0.03	0.04	0.04
	DPesticides (10^{-5}mg/kg) /MFA cycle		1.47	1.60	0.90	1.00	2.79	2.38	0.73	1.11	6.95
	volatility (Pa)		3.30	31.0	3.30	15.0	15.0	0.54	0.54	0.19	3.30
	DR (%)		39.8	43.3	45.20	43.5	29.2	25.70	31.70	30.00	27.90
Aldrin	Pesticides (mg/kg) /MFA treatment	0.05	0.03	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.04
	DPesticides (10^{-6}mg/kg) /MFA cycle		7.93	8.37	5.52	5.92	9.50	2.98	1.43	2.00	8.50
	volatility (Pa)		0.03	0.46	0.03	0.19	0.19	0.00	0.00	0.00	0.03
	DR (%)		23.7	24.9	30.6	28.3	11.2	3.40	6.90	5.90	3.70
y-chlordane	Pesticides (mg/kg) /MFA treatment	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02
	DPesticides (10^{-6} mg/kg) /MFA cycle		7.93	8.37	5.52	5.92	9.50	2.98	1.43	2.00	8.50
	volatility (Pa)		0.00	0.06	0.002	0.02	0.02	0.0001	0.0001	0.00003	0.002
	DR (%)		28.1	26.1	31.1	32.2	12.8	10.6	12	13.2	10.8
Dieldrin	Pesticides (mg/kg) /MFA treatment	0.04	0.03	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.04
	DPesticides (10^{-6} mg/kg) /MFA cycle		7.56	8.44	4.64	5.27	8.01	4.47	1.76	2.67	15.00
	volatility (Pa)		0.00	0.09	0.00	0.03	0.03	$3\ 10^{-4}$	$3\ 10^{-4}$	$1\ 10^{-4}$	$4\ 10^{-3}$
	DR (%)		25.70	28.60	29.20	28.60	10.90	6.00	9.70	9.20	7.60
Total PES	Pesticides (mg/kg) /MFA treatment	0.15	0.11	0.10	0.10	0.10	0.13	0.14	0.13	0.13	0.13
	DPesticides (10^{-5} mg/kg) /MFA cycle		3.42	3.65	2.16	2.41	4.92	3.50	1.16	1.77	10.35
	DR (%)		30	32.2	35.1	33.8	17.2	12.20	16.30	15.50	13.40

Crude Oil (mg pesticide/g oil); DR (Decontamination Ratio) = $[pest]_{-MFA}$/ $[pest]_{-RM}$ (%); CPA: Central Points (MFA1, 4, 7, 10, and 13).

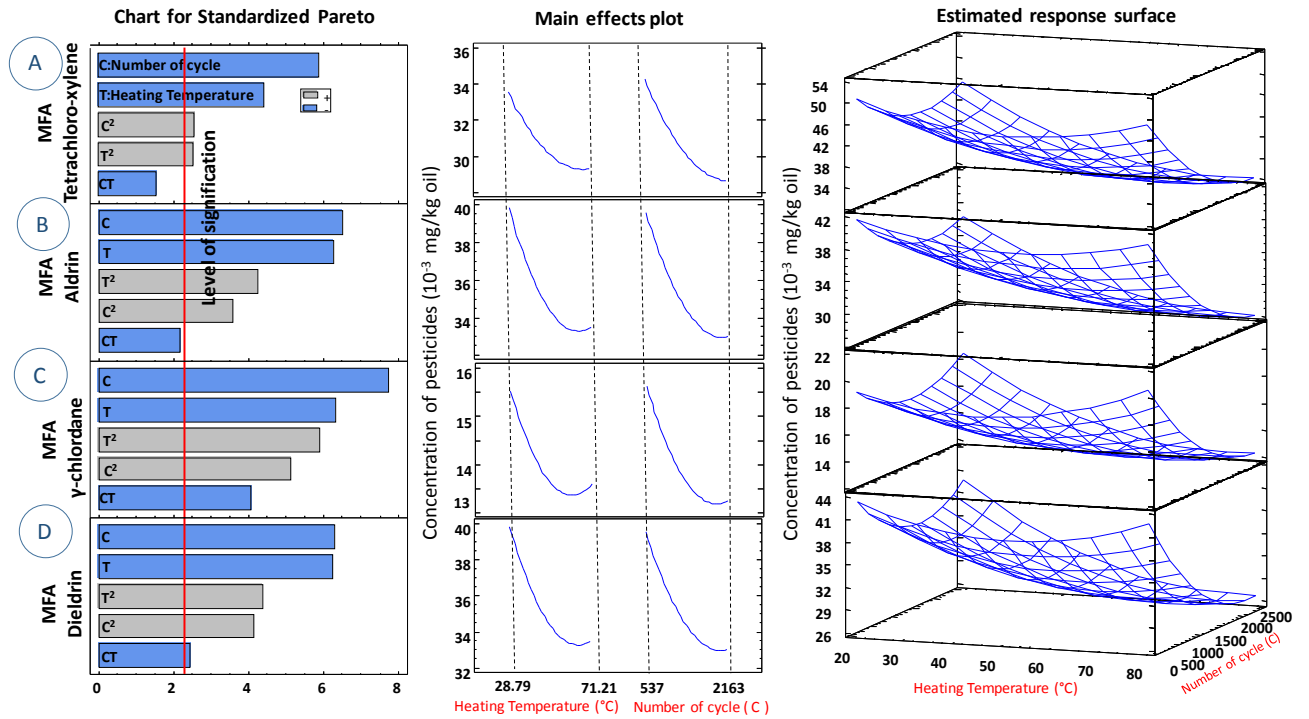

Fig-6: Pareto chart, general trends, and response surface of the effect multi-flash autovaporization MFA decontamination of organochloride pesticides (mg pest/kg oil)

The equations in Table-3 illustrated the empirical regression models of pesticide concentration as a function of the two independent variables (MFA conditions) with a regression coefficient R^2 of 90%, 94%, 96%, and 94% for Tetrachloro-m-xylene, Aldrin, γ-chlordane, and Dieldrin, respectively.

Table-2: Empirical models of concentrations of pesticide compounds versus MFA parameters

Empirical models	R^2	Eq
$[\text{Tetrachloro}] = 4.4810^{-2} - 4.7210^{-6}C - 2.4610^{-4}T + 1.5910^{-9}C^2 + 2.2910^{-6}T^2 - 6.0910^{-8}TC$	R^2=90%	Eq.1
$[\text{Aldrin}] = 4.4810^{-2} - 4.7210^{-6}C - 2.4610^{-4}T + 1.5910^{-9}C^2 + 2.2910^{-6}T^2 - 6.0910^{-8}TC$	R^2=94%	Eq.2
$[\text{Chlordane}] = 4.4810^{-2} - 4.7210^{-6}C - 2.4610^{-4}T + 1.5910^{-9}C^2 + 2.2910^{-6}T^2 - 6.0910^{-8}TC$	R^2=96%	Eq.3
$[\text{Dieldrin}] = 4.4810^{-2} - 4.7210^{-6}C - 2.4610^{-4}T + 1.5910^{-9}C^2 + 2.2910^{-6}T^2 - 6.0910^{-8}TC$	R^2=94%	Eq.4

T: heating temperature (°C); C: number of cycles; [pest]: concentration of pesticide in Crude Oil (mg pesticide/kg oil).

This variation in sensitivity or resistance of molecules to decontamination with MFA technology depended on the nature and structure of the pesticide molecules and their physicochemical properties such as solubility and saturated vapor pressure (absolute volatility).

Impact of multi-flash autovaporization MFA in the quality of crude rapeseeds oil

Impact on the Fatty acid profiles

The determination of fatty acid profiles by gas chromatography shows the presence of two major fractions, the saturated fatty acids that are palmitic acid (C16:0; 4.68%) and stearic acid (C18:0; 2.02%) and unsaturated fraction split into mono-unsaturated (64.03%) oleic acid (C18:1), and polyunsaturated contains (20.77%) linoleic acid (C18:2) and 7.69% linolenic acid (C18:3).

The study of the impact of the variation of the parameters of the multi-flash autovaporization MFA process on the variation of the fatty acid profiles represented in Table-4 clearly shows a similarity of the profiles between the samples treated and not treated with MFA (raw material) with a non-significant variation factor (less than 10%) which proves a preservation of the quality of oil after the MFA treatment.

Table-3: Impact of multi-flash autovaporization treatments on crude degummed rapeseed oil quality

	MFA parameters		Fatty acids (%)						Tocopherols (µg/g)			
Treatments	T(°C)	N- cycles	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	Beta	Gama	Alpha	Total
RM	-	-	4.68	2.02	64.03	20.77	7.69	0.52	9.28	252.16	62.73	324.17
CPA	50.0	1350	4.66	2.04	63.84	20.60	7.21	0.53	10.14	260.18	63.08	333.40
MFA2	80.0	1350	4.63	2.01	63.66	20.56	7.31	0.52	9.93	264.75	68.47	343.14
MFA3	50.0	2500	4.64	2.04	63.81	20.52	7.15	0.54	9.82	270.48	71.34	351.63
MFA5	71.2	2163	4.64	2.01	63.30	20.80	7.47	0.52	11.03	272.51	67.58	351.12
MFA6	71.2	537	4.64	2.04	63.70	20.58	7.21	0.54	10.06	264.97	64.99	340.03
MFA8	28.8	537	4.67	2.05	64.28	20.66	7.50	0.54	8.69	254.48	59.86	323.04
MFA9	28.8	2163	4.66	2.04	64.28	20.67	7.50	0.54	9.48	261.16	63.14	333.78
MFA11	20.0	1350	4.68	2.04	64.28	20.66	7.49	0.55	9.64	244.35	56.91	310.89
MFA12	50.0	200	4.67	2.05	63.95	20.68	6.80	0.54	10.40	269.61	77.90	357.90
Average of MFA treated oil			4.66	2.03	63.91	20.65	7.33	0.53	9.85	261.46	65.60	336.91
Standard deviation of MFA treated oil			0.02	0.02	0.32	0.09	0.25	0.01	0.64	8.96	6.02	14.76
Coefficient of variance			0.0040	0.0077	0.0050	0.0043	0.0345	0.0178	0.0648	0.0343	0.0917	0.0438

Impact on tocopherol Content

The chromatographic analyses of the different fractions of tocopherol in crude rapeseed oil show a dominance for the fraction ϒ-tocopherol compared to α-tocopherol, and β-tocopherol with 240.04, 65.37, and 8.38 µg/g oil, respectively.

The Table-4 represents the variation in tocopherol content in different fractions (α, β, and ϒ) following the application of different MFA treatments.

The statistical analysis represented by the analysis of variance (Anova) Table-5 & 6 confirm the non-significant effect of MFA treatments on the variation of fatty acid profiles and the content of different fractions of tocopherol. No significant difference was observed between MFA treated and untreated oil with a coefficient of variance of 0.0648, 0.0343, 0.0917, and 0.0438 for β, ϒ, and α-tocopherol, respectively. It is worth highlighting that such a similarity in tocopherol content confirms the preservation of the quality and antioxidant power of MFA treated rapeseed oils.

Table-4: Statistical analyses (Anova) of effects on changes in Fatty acid profiles.

Source		T: heating temperature	C: Number of cycles	T^2	TC	C^2	Total error	Total (corr.)
Sum of Squares	C 16:0	0.00003143	0.00024357	0.00010446	0.00202500	0.00026098	0.00260750	0.00532308
	C 18:0	0.00001250	0.00011250	0.00010446	0.00062500	0.00000880	0.00135750	0.00223077
	C 18:1	0.08900980	0.45935200	0.00376040	0.02890000	0.11441900	0.92070900	1.61269000
	C 18:2	0.00355749	0.07293280	0.00069563	0.02250000	0.00278275	0.19481000	0.29770800
	C 18:3	0.28343200	0.00827410	0.01544870	0.00902500	0.00997933	0.40473600	0.73463100
	C 22:0	0.00034357	0.00011250	0.00005261	0.00002500	0.00000043	0.00077393	0.00130769
Mean Square	C 16:0	0.00003143	0.00024357	0.00010446	0.00202500	0.00026098	0.00037250	
	C 18:0	0.00001250	0.00011250	0.00010446	0.00062500	0.00000880	0.00019393	
	C 18:1	0.08900980	0.45935200	0.00376040	0.02890000	0.11441900	0.13153000	
	C 18:2	0.00355749	0.07293280	0.00069563	0.02250000	0.00278275	0.02783000	
	C 18:3	0.28343200	0.00827410	0.01544870	0.00902500	0.00997933	0.05781950	
	C 22:0	0.00034357	0.00011250	0.00005261	0.00002500	0.00000043	0.00011056	
F-Ratio	C 16:0	0.08	0.65	0.28	5.44	0.70		
	C 18:0	0.06	0.58	0.54	3.22	0.05		
	C 18:1	0.68	3.49	0.03	0.22	0.87		
	C 18:2	0.13	2.62	0.02	0.81	0.10		
	C 18:3	4.90	0.14	0.27	0.16	0.17		
	C 22:0	3.11	1.02	0.48	0.23	0.00		
P-Value	C 16:0	0.7799	0.4453	0.6128	0.0525	0.4302		
	C 18:0	0.8069	0.4711	0.4868	0.1157	0.8373		
	C 18:1	0.4378	0.1039	0.8705	0.6535	0.3820		
	C 18:2	0.7312	0.1495	0.8788	0.3984	0.7611		
	C 18:3	0.0624	0.7164	0.6211	0.7045	0.6903		
	C 22:0	0.1213	0.3467	0.5125	0.6489	0.9518		

Table-5: Statistical analyses (Anova) of effects on variation of tocopherol content.

Source		T: heating temperature	C: Number of cycles	T^2	TC	C^2	Total error	Total (corr.)
Sum of Squares	alpha	0.564	1.117	0.011	0.235	0.189	3.196	5.328
	beta	53.832	66.380	10.316	227.557	45.226	455.423	865.428
	gamma	58.939	11.961	40.354	90.060	1.094	299.913	504.800
	total	248.431	160.302	93.359	627.252	67.354	1401.970	2622.500
Mean Square	alpha	0.564	1.117	0.011	0.235	0.189	0.457	
	beta	53.832	66.380	10.316	227.557	45.226	65.060	
	gamma	58.939	11.961	40.354	90.060	1.094	42.845	
	total	248.431	160.302	93.359	627.252	67.354	200.282	
F-Ratio	alpha	1.24	2.45	0.02	0.52	0.41		
	beta	0.83	1.02	0.16	3.50	0.70		
	gamma	1.38	0.28	0.94	2.10	0.03		
	total	1.24	0.80	0.47	3.13	0.34		
P-Value	alpha	0.303	0.162	0.879	0.496	0.541		
	beta	0.393	0.346	0.702	0.104	0.432		
	gamma	0.279	0.614	0.364	0.190	0.878		
	total	0.302	0.401	0.517	0.120	0.580		

As a short-time/high-temperature treatment, the Multi-flash Autovaporization MFA technology should preserve the quality of rapeseeds crude oil treated with similarity in the fatty acid profiles thus on the tocopherol content.

The similarity profile of untreated oils (RM) and MFA treated oils proved that MFA allows a decrease of organochlorides pesticides concertation on crude oil while preserving the oil quality with a significant conservation of the biochemical properties.

CONCLUSION

This study confirms the effectiveness of the Multi-flash Autovaporization MFA as a technology for the decontamination of pesticide traces in crude rapeseed oil. This significant reduction or elimination reached, in our work, up to 48%. However, these values would depend on the volatility and structure of the molecules. Its rate also should depend on the exchange surface and heating temperature. These feasibility aspects should be deeply studied in next research work to adequately optimize the operation. For numerous pesticides, the variation in operating parameters

(heating temperature and time or number of cycles) should significantly decrease the concentration of pesticides.

The study of the quality of the treated products proves that a MFA treatment allowed a significant decontamination of pesticides while preserving the quality and antioxidant power of contaminated products.

The present study has highlighted that the short-time/high-temperature treatment of Multi-Flash Autovaporization MFA technology is a pesticide decontaminating process perfectly adequate with heat sensitive food products.

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