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A surprising method for green extraction of essential oil from dry spices: Microwave dry-diffusion and gravity

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ABSTRACT

Without adding any solvent or water, we proposed a novel and green approach for the extraction of secondary metabolites from dried plant materials. This "solvent, water and vapor free" approach based on a simple principle involves the application of microwave irradiation and earth gravity to extract the essential oil from dried caraway seeds. Microwave dry-diffusion and gravity (MDG) has been compared with a conventional technique, hydrodistillation (HD), for the extraction of essential oil from dried caraway seeds. Essential oils isolated by MDG were quantitatively (yield) and qualitatively (aromatic profile) similar to those obtained by HD, but MDG was better than HD in terms of rapidity (45 min versus 300 min), energy saving, and cleanliness. The present apparatus permits fast and efficient extraction, reduces waste, avoids water and solvent consumption, and allows substantial energy savings.

1. Introduction

An analytical procedure for essential oil and aromas from herbs or spices comprises two steps: distillation or extraction which takes at least several hours and analysis which is finished after 15 min. Distillation or extraction is frequently done by a prolonged heating and stirring in water or solvent using Clevenger, Dean–Stark or Likens–Nikerson apparatus. This distillation consumes more than 70% of total process energy and time with high consumption of solvent [1–3]. Thus, other techniques should evolve with the aim of reducing this sample preparation step. Furthermore, with the development of the "Green Chemistry" concept "green extraction techniques" are becoming more and more attractive. Much attention has been devoted to the application of microwave dielectric heating for the extraction of essential oil such as compressed air microwave distillation (CAMD) [4], vacuum microwave hydrodistillation (VMHD) [5], microwave hydrodistillation (MWHD) [6], solvent free microwave extraction (SFME) [7], microwave-accelerated steam distillation (MASD) [8], microwave steam distillation [9] and microwave hydrodiffusion and gravity (MHG) [10]. Now, the extraction of essential oil under microwave irradiation without adding of any organic solvent or water is one of the upcoming extraction techniques that can offer high reproducibility in shorter times, simplified manipulation, reduced solvent consumption and lower energy input. There have been two reported articles in the current literature regarding "green microwave" extraction techniques of essential oil [10,11]. Microwave hydrodiffusion and gravity (MHG) have been reported by Chemat and co-workers as an efficient, economical and environmental friendly approach [10,12,13]. MHG was conceived for the extraction of volatile compounds from fresh plant materials with a minimum 60% of initial moisture [13]. It works without using any solvent or water, when microwave energy is applied, the natural water within the plant tissue heats up, distorting the plant cells, causing them to rupture and dropping by earth gravity. Also, Chemat and co-workers [11] have been recently developed another type of green microwave design: microwave steam diffusion (MSDf). It was also designed and constructed as a cleaner and eco-friendly process for the extraction of essential oil from dry plant materials. MSDf was applied for the extraction of dry lavender flowers which were submitted to a combined process of microwave irradiation and saturated steam diffusion. Microwaves distend the plant cells and the steam carrying the essential oil and drop by earth gravity outside the microwave reactor. Certainly, the most remarkable benefit of the both processes (MHG and MSDf) was their rapidity and energy saving. However, these both systems needed the presence of water, as "in situ" water in the case of MHG and saturated steam in the case of MSDf, to release the essential

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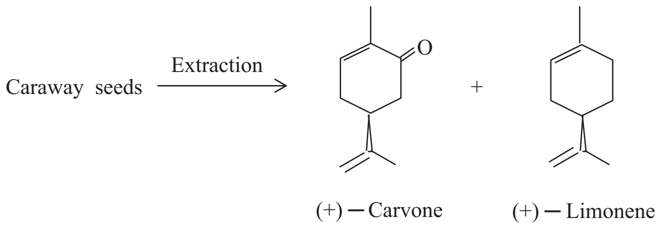

Fig. 1. Extraction of carvone and limonene from caraway seeds.

from the plant materials. To simplify these both processes, we are surprise that it can be possible to extract essential oil from dried plant materials without the addition of any solvent or water. This new and original technique has been applied to the extraction of essential oils from dried caraway seeds without any added solvent or water.

Caraway (*Carum carvi L.*) essential oil has been used as a fragrance component in cosmetic preparations including liquors, perfumes and toothpaste, while the seeds have been used as a spice and food flavouring agent [14]. Carvone and limonene are the main components (Fig. 1) with carveol, pinene, and camphene [15,16]. Recently carvone has been introduced as an effective inhibitor against sprouting, mainly in stored onions and potatoes, whereas limonene is being investigated as a raw material to produce carvone [17–19]. In practice, steam-distillation, hydrodistillation and organic solvent extraction are the most widely used procedures for the extraction of essential oil from caraway seeds. Losses of some volatile compounds, low extraction efficiency, degradation of unsaturated or ester compounds through thermal or hydrolytic effects and toxic solvent residue in the extract may be encountered using these extraction methods. Up to now, several new extraction processes have been reported for the extraction of caraway essential oil such as supercritical fluid extraction, ultrasound assisted extraction, microwave-assisted extraction and hydrodistillation by direct induction heating assisted by magnetic field (Table 1) [20–23]. The aim behind the development of these new extraction technologies was the extraction of caraway essential oil and possible improvement of its yield. Losses of some volatile compounds, low extraction efficiency, degradation of unsaturated or ester compounds through thermal or hydrolytic effects and high energy consumption solvent may be encountered using these extraction methods.

This present study has been planned with the aim to design and optimize a new and green technique for the extraction of essential oils from dried caraway seeds without any added solvent or water, just under the influence of microwave-heating and earth gravity, namely Microwave dry-diffusion and gravity (MDG) (Fig. 2). The results obtained by the optimized MDG were compared with those achieved using a conventional hydrodistillation method. We intend to make appropriate comparison in terms of extraction time, yield, aromatic composition, energy used and environmental impact. Finally, extraction mechanism was proposed to understand the action of MDG.

2. Experimental

2.1. Plants material

Caraway seeds (*Carum. carvi* L.) were purchased from a market in Avignon (France). The initial moisture content of dried caraway seeds was 7.75%. Only the dry plant material was employed in all extractions.

2.2. Microwave dry diffusion apparatus and procedure

Microwave dry-diffusion and gravity (MDG) has been performed in a Milestone NEOS microwave laboratory illustrated in Fig. 2. This is a multimode microwave reactor 2.45 GHz with a maximum delivered power of 900 W variable in 10 W increments. The extraction vessels are made from Pyrex and have a capacity of 1500 ml. Time, temperature, pressure and power can be controlled with the "easy-WAVE" software package. During experiments temperature was monitored by temperature sensor optic fibers which were inserted in the centre and outer layer of sample and also in the sample reactor. Temperature variations in different parts of plant material and reactor were measured continuously and data was saved automatically. This feedback helped in controlling the temperature by microwave power regulator.

In a typical MDG procedure at atmospheric pressure, batch of 200 g of dried caraway seeds were packed and heated into a multimode microwave reactor without added solvent or water. The direct interaction of microwaves with dried plant material favours the release of essential oils trapped inside the cells of plant tissues. The essential oil thus moves naturally downwards by earth gravity on a spiral condenser outside the microwave cavity where it condensed. The essential oil is collected, dried with anhydrous sodium sulphate and stored at 4 °C until analyzed. Extractions were performed at least three times, and the mean values were reported.

2.3. Hydrodistillation apparatus and procedure

For comparison, 200 g of dried caraway seeds was submitted to hydrodistillation (HD) with a Clevenger-type apparatus according to the European Pharmacopoeia and extracted with 1 L of water until no more essential oil was obtained [24]. The essential oil was collected, dried under anhydrous sodium sulphate and stored at 4 °C until use. Extractions were performed at least three times, and the mean values were reported.

2.4. Gas chromatography–mass spectrometry

The essential oils were analyzed by gas chromatography coupled to mass spectrometry (GC–MS) (Hewlett-Packard computerized system comprising a 6890 gas chromatograph coupled to a 5973A

Table 1
Recent publications on the extraction of caraway essential oil.

Method	Solvent	Comments	Year/reference
Supercritical fluid extraction (SFE)	CO_2	SFE (t = 45 min) compared with Soxhlet extraction ensures increase in yield of carvone with shorter extraction time.	1999 [20]
Ultrasound-assisted extraction (UAE)	n-hexane	UAE (t = 60 min) was more rapid and better in term of carvone yield than conventional system.	2004 [21]
Microwave-assisted extraction (MAE)	Hexane	MAE (t = 60 min) gives more rapid extraction and yield than conventional system.	2005 [22]
Hydrodistillation by direct induction heating assisted by a magnetic field (DIHMF)	Water	DIHMF (t = 7 h) was found more efficient than conventional hydrodistillation, with better quality of carvone/limonene.	2006 [23]

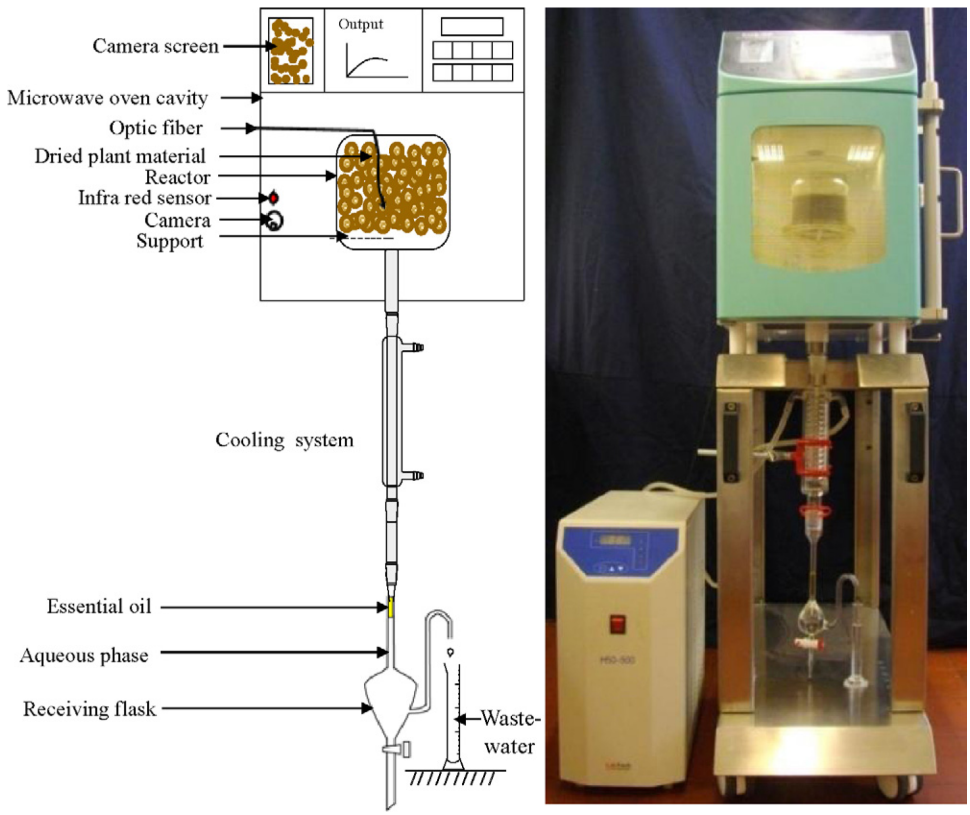

Fig. 2. Schematic diagram of Microwave dry-diffusion and gravity process.

mass spectrometer) using a fused-silica-capillary column with a polar stationary phase Stabilwax^{TM} (60 m × 0.25 mm × 0.25 μm film thickness). GC–MS spectra were obtained using the following conditions: carrier gas He; flow rate 0.7 ml min^{-1}; split 1:20; injection volume 0.1 μl; injection temperature 250 °C; oven temperature progress from 60 to 280 °C at 2 °C min^{-1}; the ionisation mode used was electronic impact at 70 eV. Most constituents were tentatively identified by comparison of their GC Kovats retention indices (R.I.), determined with reference to an homologous series of C_5–C_{28} *n*-alkanes and with those of authentic standards available in the authors' laboratory. Identification of the components was achieved from their relative retention indices on DBWAX column, determined with reference to a homologous series of C_5–C_{28} *n*-alkanes, and by a comparison of their mass spectral fragmentation patterns with those stored in the data bank (Wiley/NBS library) and the literature [25].

2.5. Scanning electron microscopy (SEM)

Single seeds were fixed on aluminium support and sputter coated with gold. The specimens were examined with a FEI-Philips XL30 scanning electron microscope, under standard vacuum condition and secondary electron detector.

3. Results and discussion

3.1. Preliminary study

Different microwave irradiation power, 50, 75, 100, 150 and 200, were examined. Fig. 3 shows the total extraction time (it was until no more essential oil was obtained) as function of the microwave power. A microwave power of 100 W was chosen as an optimum of power which permits the complete extraction of caraway essential oil in 45 min.

3.2. Kinetics microwave extraction

As shown in Fig. 4 MDG is clearly quicker than conventional HD, an extraction time of 45 min with MDG provides yield comparable to that obtained after 300 min by HD, which is one of the reference methods in essential oil extraction. The overall yield of essential oils obtained from caraway seeds was 2.59% and 2.54% by MDG and HD, respectively.

Four phases are observed in the process of extraction kinetics, for both techniques (see Fig. 4I and II), with different behaviour profiles. Fig. 4I was a typical sinusoid extraction curve obtained by MDG showing the following four steps:

- Step (A) corresponding to the time necessary for heating the dried plant material. It is also the time necessary

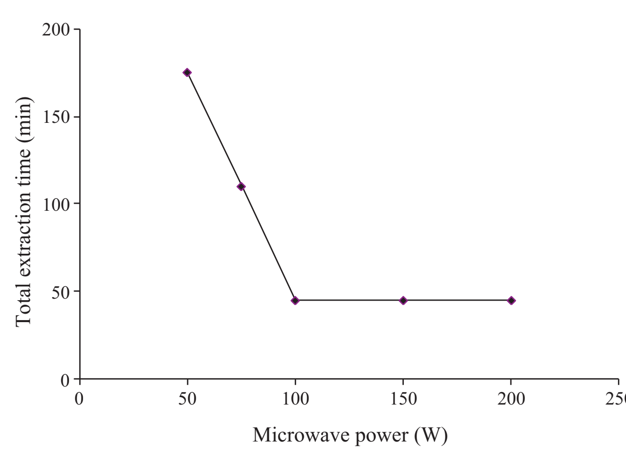

Fig. 3. Microwave power profile as a function of total extraction time with MDG.

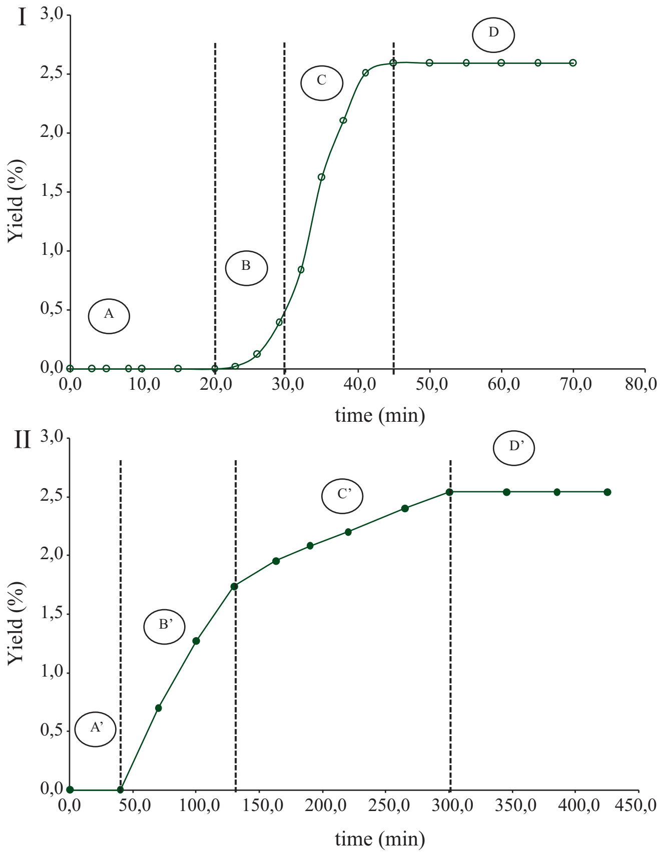

Fig. 4. Yield profiles as a function of time for the MDG (○) and HD (●) extractions of essential oil from caraway seeds. (A) and (A′): Time necessary for heating the plant materiel; (B) and (B′): beginning of extraction recovery; (C) and (C′): increase of the yield; (D) and (D′): the end of the extraction process.

to have the first droplets getting outside the microwave cavity.

- Step (B) is represented by the curvilinear branch, which characterizes the first quantities extracted, and corresponds to approximately 13% of the totally yield.
- Step (C) is represented by an increasing line, which characterizes the rapid increase in the yield and representing approximately 96% of the totally yield.
- Step (D) corresponds to a horizontal line which marks the end of extraction process.

The profile of HD (see Fig. 4II) also presents the four phases but different to those obtained with MDG. The first part (A′) corresponding to the time necessary for heating the plant materiel with water. The second part (B′) leading to 68% of the yield obtained into 130 min. The end of the extraction is reached after 300 min.

3.3. Composition of essential oil

Table 2 lists the grouped compounds in caraway essential oil: oxygenated and non-oxygenated fractions and composition of chemical families obtained by both methods. The same number of volatile secondary metabolites was found in the essential oils with similar relative amounts. The oil consists of two main components, both monoterpenes: carvone and limonene, with equivalent relative amounts for both extraction methods: 66.89–67.59% and 30.30–30.10%, respectively, for HD and MDG, the remainder consisting of other minor and trace substances in the oil.

3.4. Temperature profiles

In order to understand the behaviour of MDG, the influence of temperature on the extraction kinetics of caraway essential oil was examined. Fig. 5 shows a typical temperature profiles during MDG and HD extraction. In the case of MDG, the temperature rises to the boiling point of water which marks the first droplets of extract. When there is no essential oil to extract the temperature increases very quickly (from +150 °C to +200 °C) and marks the end of the extraction. Yet, for HD (see Fig. 4II) two phases are observed in the process of temperature extraction. The first part (1′) is represented by an increasing line until the temperature reached 100 °C and thus the distillation of the first essential oil droplet is obtained. In the second part (2′), the extraction temperature is equal to boiling temperature of water at atmospheric pressure (100 °C) until the end of extraction.

Table 2
Chemical compositions of caraway essential oils obtained by HD and MDG.

No.	Compounds	RI	HD	MDG
	Monoterpenes		30.59	30.68
1	α-Pinene	1023	0.02	0.01
2	Sabinene	1121	0.01	0.02
3	3-Octanone	1253	0.02	0.20
4	Myrcene	1165	0.15	0.16
5	*p*-Cymene	1268	0.03	0.04
6	Limonene	1206	30.30	30.10
7	(*E*)-β-Ocimene	1282	0.02	0.08
8	γ-Terpinene	1285	0.04	0.07
	Oxygenated Monoterpenes		67.64	68.67
9	Linalool	1538	0.07	0.12
10	(*Z*)-*p*-2,8-menthadien-1-ol	1670	0.07	0.07
11	(*Z*)-Limonene oxide	1449	0.12	0.15
12	(*E*)-Limonene oxide	1458	0.07	0.08
13	Dihydrocarvone	1560	0.20	0.22
14	Carveol	1850	0.25	0.28
15	Carvone	1723	66.89	67.59
16	Piperitone	1680	0.08	0.08
17	Perillaldehyde	1783	0.05	0.08
	Sesquiterpenes		0.20	0.20
18	(*E*)-β-Caryophellene	1594	0.20	0.20
	Total oxygenated compounds (%)		67.64	68.67
	Total non-oxygenated compounds (%)		30.79	30.88

RI: linear retention indices relative to C_8–C_{22} *n*-alkanes on Stabilwax™ capillary column.

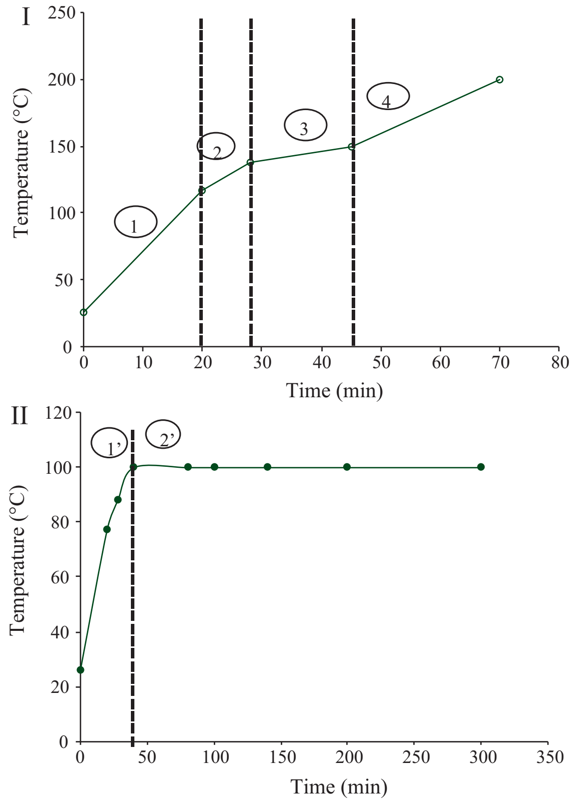

Fig. 5. Temperature profiles as a function of time during MDG (○) and HD (●) extractions of essential oil from caraway seeds.

3.5. Proposed MDG mechanism

To explain if 'in situ' water favours the release of essential oils trapped inside the cells of plant tissues, we make appropriate comparison in terms of the presence and absence of 'in situ' water allows the MDG extraction.

Case 1: Caraway seeds dried on a bench in the shade (presence of the 'in situ' water).
Case 2: Caraway seeds dried in electric oven at 60 °C (evaporate the 'in situ' water).

Fig. 6 was a typical extraction curve obtained by both experiences, at optimal operating conditions (100 W), which shows the variation in the extracted yield according to the extraction time. The result suggests that the behaviour of both curves was similar and the differences were found only in oil yield and in extraction time. The absence of 'in situ water' gives approximately 80% of total yield. So essential oil's components such as carvone (Bp 235 °C) and limonene (Bp 175 °C) could be extracted or evaporated without "in situ" water. Thus, we can suggest that the extraction mechanism of essential oil obtained by MDG is partly due to internal heating of essential oil molecules under microwaves irradiation from the inside to the outside of caraway seeds without the action of "in situ" and partly due to a synergy combination of the two transfer phenomena mass and heat acting in the same direction.

3.6. Microhistology analysis

The various extraction methods produced distinguishable physical changes in the caraway seeds. Fig. 7 is a micrograph of the untreated seeds, which can be compared with structures of the treated seeds. After microwave extraction, Fig. 7 shows that cells and cell walls have been affected to different degrees. We observed a huge perforation on particles' external surface of and some rubbish and starch are dispersed. In other part, 300 min of conventional hydro-distillation have resulted in clear cell forms and most of the cell walls were opened as observed in Fig. 7. Some parts are still filled with intact oil glands and/or fat. At the end of the control experiment, the cell walls seems more thicker but intact and most of the cells were totally free from any component released out of the cell with a little left starch which is in accordance with Brun et al. [26] who noticed the complete absence of any form of rupturing of the cuticular layer during steam distillation and hexane extraction of plant material.

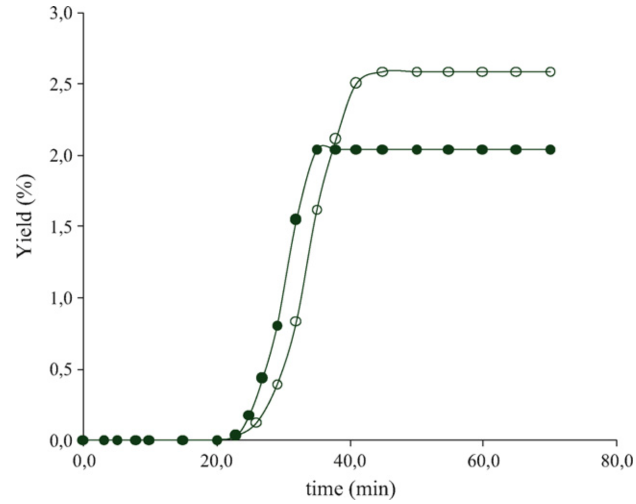

Fig. 6. Yield profiles as a function of time for MDG extraction from normal caraway (○) and dried caraway (●).

The changes observed for MDG were markedly different from those observed by control HD, showing that all the cell walls are finally broken and damaged and have resulted into non-significant cell shapes. There was a clear evidence of the explosion said by Pare and Belanger [27] to occur at the cell level as a consequence of the sudden temperature rise, generated in that case by located hot spots caused by microwave power. When the glands were subjected to more severe thermal stresses and localized high pressures induced by microwave heating, the pressure build-up within the glands could have exceeded their capacity for expansion, and caused their rupture more rapidly than in control experiment. This was the mechanism postulated by Pare and Belanger [27] and Chen and Spiro [28] for the microwave extraction of rosemary leaves in hexane.

3.7. Cost, cleanliness, scale-up and safety considerations

MDG is proposed as an "environmental friendly" extraction method for the extraction of secondary metabolites from dried plant materials. The reduced cost of essential oils extraction is clearly advantageous for the proposed MDG method in terms of energy and time. Conventional procedure (HD) required an extraction time of 300 min. The MDG method required only 45 min. The energy required to perform the two previously described extraction methods are, 163 kWh kg^{-1} essential oil for HD and 102 kWh kg^{-1} essential oil for MDG. The power consumption has been determined with a Wattmeter at the microwave generator entrance and electrical heater power supply. Regarding environmental impact, the calculated quantity of carbon dioxide rejected in the atmosphere is higher in the case of HD (130 kg CO_2 kg^{-1} of essential oil) than for MDG (82 kg CO_2 kg^{-1} of essential oil). These calculations have been

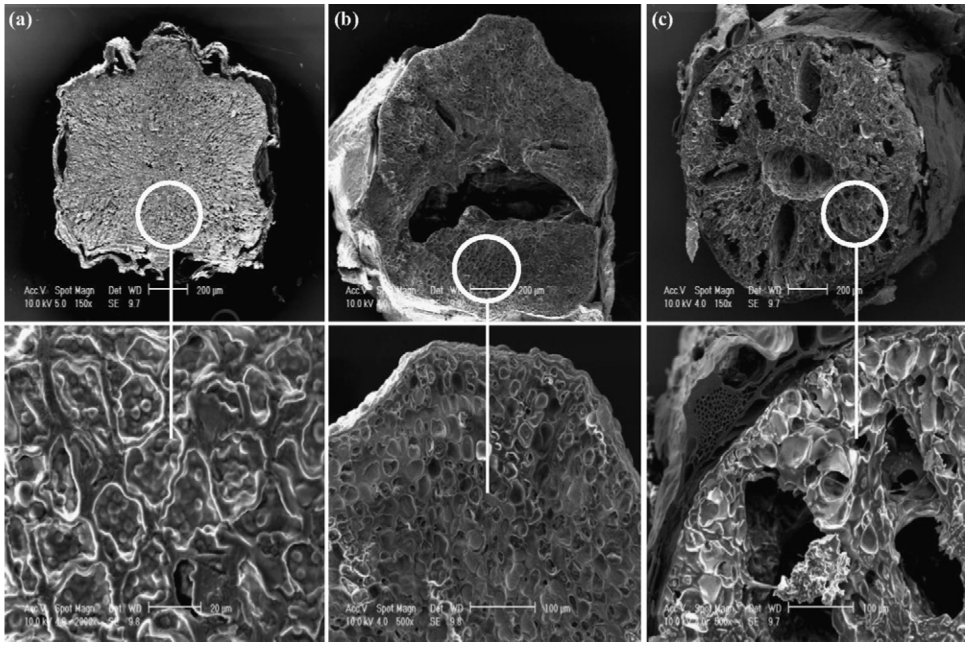

Fig. 7. SEM micrographs showing the morphology of untreated caraway seeds (a), after HD extraction (b), after MDG extraction (c).

made according to the literature: to obtain 1 kWh from coal or fuel, 800 g of CO_2 will be injected in the atmosphere during combustion of fossil fuel [29].

4. Conclusions

A new and green process for the extraction of essential oil was developed in this paper: Microwave dry-Diffusion and gravity (MDG). The MDG process has been studied using dried caraway seeds. This new alternative offers important advantages over traditional hydrodistillation, namely; shorter extraction times (45 min versus 300 min for HD), less energy consuming and lower cost. The new systems developed indicate that microwave extraction in combination with dry-diffusion and gravity offers numerous advantages in term of yield and selectivity, with better extraction time, essential oil composition, and is environmentally friendly.

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