Hydrodistillation of caraway by direct induction heating assisted by a magnetic field process

L. Lagunez Rivera¹* and G. Vilarem²

1 Instituto Politécnico National, CIIDIR-Oaxaca, Hornos No. 1003, Sta. Cruz Xoxocotlan, Oaxaca, C.P. 71230, México.
2 Laboratoire de Chimie Agro-Industrielle, Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques, Institut National Polytechnique de Toulouse, Unité Mixte de Recherche 1010 INRA/IPN-ENSIACET, 118 route de Narbonne, 31077 Toulouse Cedex 4, France

Received 20 September 2005; Revised 19 September 2006; Accepted 23 October 2006

ABSTRACT: This paper presents the development of a new method of hydrodistillation of the essential oil of caraway (Carum carvi L.) by direct induction heating assisted by magnetic field (DIHMF) and the development of the required apparatus. Water and food salt (99.8% sodium chloride) were used as electrolyte solutions and at the same time as an extractant solution. The method was tested on caraway fruits as a source of carvone and limonene as the main components. The essential oil of this fruit was also isolated by conventional hydrodistillation as a standard method on both laboratory and pilot scale. The isolated volatile products obtained by the two methods were analysed using gas chromatography (GC). The obtained results were then compared. Even though DIHMF hydrodistillation ensures the isolation of the essential oils as well as conventional hydrodistillation, the time required to obtain the isolated products is remarkably shorter. Copyright © 2007 John Wiley & Sons, Ltd.

KEY WORDS: hydrodistillation method; essential oil; caraway; limonene; carvone; direct induction heating; magnetic field

Introduction

Flavour and fragrance components are normally isolated and concentrated using distillation, extraction and adsorption.²⁻⁶ In general, different types of distillation are the most widely used procedures for the isolation of essential oils from aromatic plants. Hydrodistillation at atmospheric pressure is the most frequently used method of distillation.¹ The advantage over other isolation methods, e.g. extraction, is that isolation by distillation includes only volatile compounds.²³

Simultaneous distillation–extraction was studied by Likens and Nickerson,⁴ who first reported the extraction of plant volatiles using solvents. They also used this process to isolate volatile compounds directly from the plant material or to separate them from dilute aqueous solutions obtained by hydrodistillation. Subsequent studies on extraction have been carried out on aromatic plants.⁶⁻⁷ The disadvantage of all of these methods is the partial loss of volatile compounds during removal of the excess solvent and their pollution with non-volatile components from the sample and the solvents.

In general, extracting natural products from plants using supercritical CO₂ (carbon dioxide) shows a high affinity not only to essential oil components but also to other classes of non-volatile compounds, such as cuticular waxes, fatty acids, colouring agents and resins.²⁻¹⁴ Supercritical CO₂ offers unusual possibilities for a selective extraction due to control via solubility and manipulation of its pressure and temperature.¹ There have been a number of studies on caraway fruits (Carum carvi L.),⁶⁻⁷ which have reported a marked difference in the components isolated. Among supercritical fluid extraction (SFE), ultrasound-assisted extraction and distillation methods, the yields are slightly lower using SFE.

The composition, and thereby the quality, of the essential oil of a selected plant species mainly depends on the nature of the raw material used and the method of isolation employed. In distilled oils, differences in oil quality are more likely to arise from variations in distillation time, rate of distillation, efficiency of steam condensation and separation methods.¹⁵⁻¹⁶

The process of direct induction heating assisted by magnetic field (DIHMF) is based on Ohmic heating. It consists of applying a voltage to the terminals of two electrodes, causing an ionic movement by the action of an AC voltage difference that leads to heating of the solution. Three main phenomena, electric, thermic and hydrodynamic, are present and are mutually coupled. The
electric energy brought to the product is transformed into thermal energy by the Joule effect. The efficiency of this type of heating is influenced by the nature of the electrolyte solution and its physical and electrical properties. The energy is directly generated at the core of the material to be distilled. The aqueous solution of food salt (99.8% sodium chloride) is considered as an electrolyte and it greatly increases the electric conductivity when the temperature increases.

The hydrodistillation of caraway by the DIHMF process was developed as an alternative method for the isolation of essential oils. The aim of this paper is to show the new apparatus and the method developed, as well as to report some advantages of this isolation method, which can greatly reduce the time of extraction and obtain isolated products containing neither toxic solvent residues nor non-volatile compounds.

**Experimental**

**Plant Material**

The caraway fruits which were used as the raw material were obtained from Alp’Erbo S.A. (France). The dried fruits (7% humidity) were weighed and directly introduced into the extraction apparatus.

**Reagents**

The reagents GC grade (+)-carvone, (+)-limonene and cyclohexane were purchased from Aldrich. Food salt (99.8% sodium chloride) was obtained from Gaches-Chimie (France). All reagents were used as received.

**Isolation of Essential Oils by Conventional Hydrodistillation on a Laboratory Scale**

Caraway fruits were immersed in 4 l of 0%, 6% and 12% aqueous food salt solution, with 1:20, 1:10 and 1:6.7 fruits:distillation medium ratios, and heated under mechanical stirring until boiling point (105 ± 1 °C) under atmospheric pressure. Hydrodistillation was conducted for 7 h using a classical Schilcher\textsuperscript{19} apparatus.

**Isolation of Essential Oils by Conventional Hydrodistillation on a Pilot Scale**

The raw material was submitted to a pilot-scale hydrodistillation for 7 h, using a hydrodistillation system (Tournaire S.A., France). Experiments were performed at boiling temperature, atmospheric pressure, under stirring at 15 r.p.m. Different experimental batches of 150 l, with 1:21.4, 1:10 and 1:7.2 fruits:distillation medium ratios and aqueous solutions of 0%, 6% and 12% w/w food salt, were used.

**Apparatus for Essential Oil Isolation by the DIHMF Process**

The apparatus shown in Figure 1 consists of a cylindrical receptacle of 50 l (A), which has an internal diameter of 40 cm and a height of 60 cm, with an inner closed canal of 20 cm in diameter and a height of 55 cm. The inductor (B) was inserted into the inner canal of the container. On the top side of the reactor, there is a lid (C) with four outlets. A 1 cm thick plastic joint (D) is inserted between the cylindrical receptacle and the lid. The lid and the container are joined together by a Teflon clip. The distillation columns (E), which have an internal diameter of 5 cm and a length of 50 cm, were connected to the two outlets of the lid and the end of the column is inserted up to 4 cm inside the Teflon elbow (F), the other side of the Teflon elbow is connected with the condenser (G). At the other extremity of the condenser is situated the decantation system (H) which has a capacity of 4 l.

The operational capacity of the inductor is 35 kW at 20–50 kHz of operational frequency from a power source (I) generated from 400 V. The polarity of the aqueous solution and its electric power are the sources of heat inside the reactor. The cylindrical receptacle was filled to 301 of an 6% aqueous solution of food salt. Then, the electric power of the induction system was brought up to the working power of 7 kW. The 8 kW power inside the reactor is generated with a frequency of 38 kHz. Within the solution, the heat is generated by means of a magnetic field mechanism. The fruits were introduced directly into the cylindrical receptacle, immediately reaching the boiling point at 105 ± 1 °C. While boiling, the saturated vapour bearing volatile compounds was carried through the two distillation columns integrated in the reactor. The vapour finally passed to the condensers to be cooled and condensed at a distillation rate of approximately 3.6 l/h. For the hydrodistillation process, the volume was adjusted by means of a liquid feeding tube (J). Adjustments were made with water. This was fed by the action of a peristaltic pump (K; Gilson Minipuls3, Model M312). At the same time, the conductivity of the aqueous solution in the reactor was measured with each change of electric power. This measurement was made by a conductimeter 340i (L) with a standard conductivity cell TetraCom 325, by means of a system prepared with a tube (M) submerged in the reactor solution, connected at its upper end to a recirculation tube (N), which allows the aqueous solution of the reactor to be carried to the conductimeter cell on the outside, by means of the action of the peristaltic pump (O; LMSTECHNIK). After measuring the conductivity of the solution, it was returned to the reactor by the same system, but in reverse order. At the same time, a manometer (P) was installed, which indicated any changes in pressure if these were to occur in the reactor.

This apparatus ensures the hydrodistillation of the plant material and the concentration of volatile compounds in a pilot scale. It is known that increasing the electric power or the concentration of sodium chloride can accelerate the hydrodistillation of volatile compounds. In this case, the electric power and the sodium chloride concentration are approximately constant during the hydrodistillation process. To isolate the essential oils from caraway fruits by this method, an aqueous solution of food salt was selected as a suitable solvent.
Essential oils were isolated from 3 kg caraway fruits for 7 h with 30 l of the aqueous solution. After hydrodistillation, the essential oils were analysed by GC. Prior to analysis, the essential oils were refrigerated.

Gas Chromatography

GC analysis was performed using a Hewlett-Packard gas chromatograph, HP 5890 II, equipped with a flame ionization detector and a HP 6890 autoinjector. The separation was made on vf5 Varian capillary columns (30 m × 0.25 mm i.d., film thickness 0.25 mm). The oven programme started at 90 °C, rising at a rate of 2 °C/min to 210 °C; injector and detector temperature, were 200 °C and 230 °C, respectively; carrier gas, helium at a flow rate of 1.3 ml/min. The hydrodistilled extracts were diluted 10 times and 0.5 µl diluted solution was injected into the GC with the same split ratio of 1:100. The calibration factors for limonene and carvone were determined by external standards of two independent samples containing each 100 and 200 p.p.m. of these compounds dissolved in cyclohexane.

Results and Discussion

The apparatus presented has a homogeneous heating system. It is necessary to take into account the influence of the heating currents in the vapour phase and the influence of the currents occurring for the electrical conductivity of the aqueous solution. Tests have shown that the conductivity of the aqueous solution at 6% of food salt can create a displacement of ions and an exchange of electrons between the electrodes and the free ions of sodium chloride (Figure 2). In the sodium chloride the conductivity rises strongly with the temperature. At the same time, this temperature changes as a function of the electric power and the frequency generated in the apparatus by DIHMF. The direct induction heating technique offers a solution by directly inducing currents in this electrolyte. The energy is directly generated at the core of the material to be extracted.

Isolation and concentration of volatile compounds are performed by a single process of hydrodistillation. At the same time, the hydrodistillation is developed in various...
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Figure 2. Variation of electric conductivity of aqueous solution to 6% food salt (99.8% sodium chloride) in the interior of the reactor by DIHMF, as a function of temperature; at the same time, this temperature changes in function according to the electric power and the frequency.

Table 1. The yield and composition of essential oils obtained from caraway fruits at the end of the extraction by the DIHMF process and conventional hydrodistillation on a laboratory scale (Schilcher18 apparatus) and on a pilot scale to different parameters tested.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Fruits/H2O: NaCl ratio</th>
<th>NaCl concentration (%)</th>
<th>Essential oil yield (g/100 g fruits)</th>
<th>Carvone: limonene ratio</th>
<th>Compound (g/100 g essential oil)</th>
</tr>
</thead>
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<tr>
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<td></td>
<td>Limonene</td>
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<td>Conventional</td>
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<td>hydrodistillation (Schilcher18 apparatus)</td>
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<td>2.58</td>
<td>5.68</td>
<td>3.6</td>
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<td></td>
<td>1:20</td>
<td>6</td>
<td>3.2</td>
<td>5.56</td>
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<td></td>
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<td>3.2</td>
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<td>2.01</td>
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<td></td>
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<td>3.93</td>
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<tr>
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<td>3.5</td>
<td>3.93</td>
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<td>by magnetic field processes</td>
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<td>3.93</td>
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<tr>
<td></td>
<td>1:10</td>
<td>10</td>
<td>hydrodistillation becomes violent and out of control</td>
<td>10.68</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Results presented are the means of three replicative isolations.

stages: diffusion, evaporation, condensation and separation of the oil and aqueous phases of the condensate. Table 1 shows the influence of the plant material:aqueous solution ratio and of the content of the conductive NaCl solution on the outcome, and the relative composition of the essential oil. The results show that the difficulty in extracting the essential oils increases with higher contents of NaCl in the solution. If the essential oil yields are checked, it is noticeable that the higher the NaCl content in the extractive solution, the lower the yield in essential oil. From a qualitative point of view, the effects of the NaCl content on the chemical composition of limonene and carvone are also seen. The chromatographic analyses show that the concentration of limonene decreases with higher NaCl contents, while the concentration of carvone increases. DIHMF-assisted tests at 3.5% NaCl yield twice as much for the hydrodistillation. At 10% and 12% NaCl, the hydrodistillation with DIHMF becomes violent and out of control: thus, the best compromise under our working conditions is 6% NaCl. The 1:10 plant material:conducive solution ratio has been selected because it leads to better distillation outcomes on the DIHMF-assisted hydrodistillation system. The extraction rate and the yield of essential oil depend on the methods of hydrodistillation. The DIHMF hydrodistillation method has been compared with conventional hydrodistillation as an alternative in terms of rapidity and quality. The essential oil yield as a function of hydrodistillation time is
shown in Figure 3. The yield increases quickly at the beginning of the extraction, its evolution becoming slower thereafter. Moreover, after 3 h of DIHMF hydrodistillation, more than 88% of the essential oil was recovered, whereas for the conventional hydrodistillation, 5 h are required to extract 80% of the essential oil. Hydrodistillation on a laboratory scale using a Schilcher18 apparatus takes 3 h and produces less than 80% of essential oil. Generally, the quantity of essential oils is lower on a pilot scale than on a laboratory scale.15 However, under our working conditions the most efficient method with regard to distillation rate is the DIHMF hydrodistillation method.

The means of three replicate isolations of the yield of essential oil obtained by DIHMF hydrodistillation at the end of the extraction was 2.11 g/100 g of fruits, respectively, for conventional hydrodistillation, 2.03 g/100 g of fruits for the pilot scale distillation and 2.58 g/100 g of fruits for laboratory scale distillation (Schilcher18 apparatus). The compositions of the essentials oils obtained by DIHMF hydrodistillation and conventional hydrodistillation are not qualitatively different, but they do differ quantitatively. Two compounds were analysed in the essential oil of caraway; carvone and limonene as the principal components. The carvone:limonene ratio at the end of the extraction was 11.51 by DIHMF hydrodistillation and 3.93 and 4.02 by conventional hydrodistillation pilot scale and laboratory scale distillations, respectively.

DIHMF-assisted hydrodistillation seems to increase the polarity of the carvone. Hydrophobic parts of the molecules seem to be reduced in the presence of a magnetic field. Thus, increasing the polarity helps the hydrodiffusion from the inside of the ‘fruit’ to the distillation medium. This hypothesis matches the studies by Colic et al.19–21 and OseKi.22 The hydrodiffusion phenomenon can also be increased by the size diminution of the aggregates of water molecules in magnetic fields.23 It is also probable, in the specific case of the caraway fruit, that part of the carvone is synthesized from limonene or other metabolites24 or by the oxidative dehydrogenation of carveol, according to the method by Wacker.25

By analogy with the results from studies of hydrodistillation of dill seeds26 and fruits of caraway (Carum carvi L.)27 under microwaves, DIHMF hydrodistillation has similar effects to those under microwaves, for the selectivity in extraction of carvone is outstanding. However, at the cellular level, DIHMF effects resemble more closely those of ultrasound,28 where the cellular content of the fruits of caraway distilled under DIHMF has disappeared, as shown in the scanning electron micrograph (SEM) in Figure 4.

The most efficient method in terms of chemical composition of the extract seems to be DIHMF hydrodistillation, as can be seen in the Table 1 of the extracts obtained by the two methods, but it will be necessary to widen the range of these studies to other plants and organs in order to assess the advantages of DIHMF-assisted hydrodistillation.

**Conclusion**

Extended periods of distillation adversely affect the essential oil quality and also the cost of distillation, while the method of hydrodistillation by DIHMF ensures the isolation of the essential oil as efficiently as conventional hydrodistillation. In addition, the extraction time is much
shorter and the quality seems better in terms of carvone production (carvone:limonene ratio, 11.51). The cause may be the increase of the polarity of carvone in the electromagnetic field, which favours its selective extraction, or a transformation of limonene into carvone with, probably in this case too, an intervention of the electromagnetic field. Under DIHMF, the magnetic field may have the effect of increasing the hydrodistillation speed, by increasing the hydrodiffusion from either the ionization of the extraction medium or reduction of the size of the water aggregates.

Note—These results are part of the studies of L.L.-R., achieved with the DIHMF test equipment, particularly in order to extract essential oils from other plants and other plant fractions (dyestuffs, polysaccharides, etc.).

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