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Swelling of plant material in supercritical carbon dioxide

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ABSTRACT

Swelling of plant material belonging to several plant families and the influence of swelling on supercritical fluid extraction process were investigated in this study. While swelling of Lamiaceae family species as well as hop cones and pellets occurred during the exposure of plant material to supercritical carbon dioxide, swelling of valerian root and ginger rhizome happened after the decompression step. Optimal pretreatment of herbaceous matrix which will enable commencement of continuous extraction from already swollen plant material was defined on the basis of swelling test results. Experimental results were modeled and energy savings due to the optimal processing on the laboratory scale were calculated. Sorption of carbon dioxide into the hop pellet was measured and the diffusion coefficient in the solid phase was determined. Obtained results indicated that the effective diffusion coefficient in the hop pellet was increased by one order of magnitude due to swelling.

1. Introduction

Exposure of herbaceous matrix to supercritical fluid leads to partial dissolving of plant material in compressed gas, which may cause changing of tissue properties and accordingly the plant tissue itself might be subject to swelling. The extent to which changes occur depends on the specific structure of plant material, as well as on the operational conditions (pressure and temperature). The time of exposure to supercritical fluid might also influence the swelling process. Swelling of plant material could lead to increased effective diffusion coefficient that would allow faster diffusion through the porous structure of plant material's particle in a supercritical fluid extraction (SFE) process. Hence, if the continuous SFE process starts from already swollen plant material, some amount of supercritical fluid could be saved. Up to date swelling of polymer materials exposed to supercritical CO_2 was the subject of reported investigations [1–4]. Since the polymers are used as tubing or sealing materials in a number of technical applications in contact with compressed gasses, it is essential to know how the pressurized gas influences the polymer properties.

The aim of this work was to analyse the influence of exposing plant material of several families to supercritical carbon dioxide on plant material properties and SFE process. The influence of process parameters, such as pressure, temperature and time of exposure, on the swelling of plant material was analyzed as well. Lamiaceae family species (mint, wild thyme, hyssop, sage and rosemary), valerian root, ginger rhizome and hop cones and pellets were chosen for the study. In the case of Lamiaceae family species, valerian root and ginger rhizome, benefits of swelling behavior on the SFE process were demonstrated. Lamiaceae family species are characterized by peltate glands (type of glandular trichomes) as seats of essential oil production and storage. Peltate glands are placed at the very surface of the leaves. Previously published investigations [5–7] indicated peltate glands cracking due to the exposure to supercritical fluid. Therefore swelling effects on the SFE of essential oils were investigated and discussed in this study. Influence of swelling on the SFE from Lamiaceae family species at higher pressures was investigated as well. Sage and rosemary were chosen for this investigation because of the well known antioxidant properties of their fractions obtained at higher pressures [8–11]. Valerian root and ginger rhizome are characterized by small secretory cells placed within the plant tissue. In the case of valerian secretory cells are determined to be 8 μm in diameter [12]. Diameter of ginger secretory cells is somewhat larger and its average value was determined to be 20 μm [13]. Possibility of the SFE from secretory cells enhancement by the plant tissue swelling before the continuous extraction was tested in this study. The SFE experimental results were subjected to mathematical modeling. The influence of plant material swelling was analyzed through the values of the model parameters, namely those indicating diffusion through the particle of plant material.

As the hop is one of the most important raw materials in the industrial SFE processing, hop cones and pellets were also

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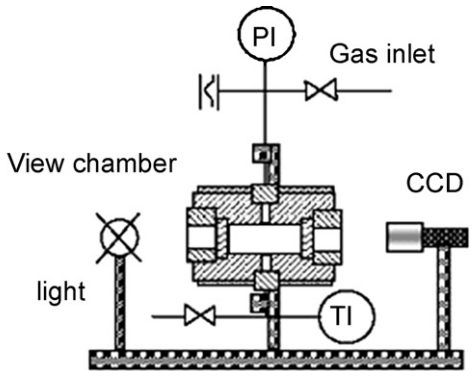

Fig. 1. Schematic presentation of high-pressure view chamber.

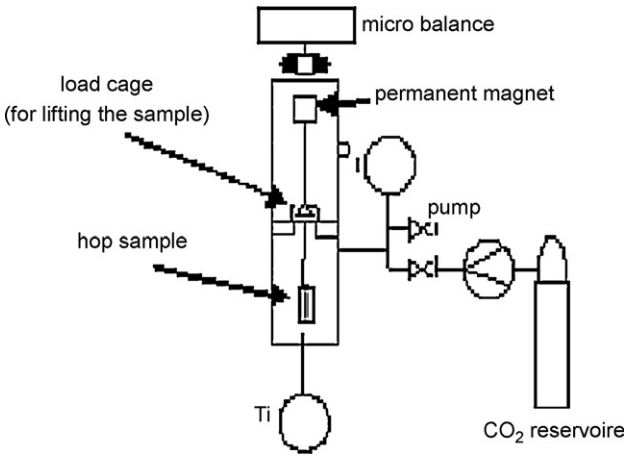

Fig. 2. Schematic presentation of high-pressure view chamber with gravimetric measuring device.

chosen for the swelling investigation. Sorption of carbon dioxide into the hop pellets used in industrial facilities was measured as well.

2. Materials and methods

2.1. Materials

Leaves of hyssop (*Hyssopus officinalis*), wild thyme (*Thymus serpullum*), mint (*Mentha piperita*), rosemary (*Rosmarinus officinalis*), sage (*Salvia officinalis*), hop (*Humulus lupulus*) as well as dry root of valerian (*V. officinalis* L - cultivar Arterner züctung as well as wild grown valerian) and ginger (*Zingiber officinalis*) rhizome were used in experimental studies. Hyssop, rosemary and wild thyme were cultivated in the southern Balkan region. Mint and Valerian were cultivated in the northern Serbia and ginger rhizome was imported from China. Hop cones (type Marynka and Magnum) and pellets produced from Marynka and Magnum milled cones, that are exploited in the industrial facilities were supplied from the Fertlilizers Research Institute, Pulawy, Poland. Commercial carbon dioxide (99% purity, Tehno-gas, Novi Sad, Serbia) was used for the extractions.

2.2. Swelling detection

Swelling of plant tissues was analyzed and detected optically inside a high-pressure view chamber (Pmax = 35 MPa, Tmax = 200 °C) purchased from Eurotechnica and presented in Fig. 1. A solid sample was placed inside the chamber by opening the sapphire windows. The chamber was pressurized by CO_2 and the optical properties were recorded by means of a CCD-camera containing a zoom lens. CCD-camera is connected to a PC. Plant tissues of mint, valerian, ginger and hop were examined. A relative size change (d/d_0) of the plant material was determined. The experimental conditions under which the plant material was pressurized by supercritical carbon dioxide are presented in Table 1.

Table 1
The conditions of swelling experiments.

Herb	Pressure (MPa)	Temperature (K)
Mint	10	40
Valerian	15	50
Ginger	28	60
Hop pellet	10/15/29	50
Hop cone	25	40

2.3. Sorption of CO_2 into hop pellets

A high-pressure gravimetric measuring device (Rubotherm, Germany) connected to a high-pressure view chamber (Pmax = 35 MPa, Tmax = 120 °C, Eurotechnica, Germany) for quantifying weight under elevated CO_2 pressure and simultaneously observing phase behavior was used for determination of the sorption kinetics and isotherms. Pelletized hop (Magnum, moisture 9.1%) was pressed into a cylindrical glass containment of about 6.5 mm diameter. The glass containment is connected to the permanent magnet inside the view chamber which on its turn is pressurized with CO_2. The actual weight of the containment including the hop results from the difference between its mass and the buoyancy at the respective conditions of temperature and pressure. This weight is detected via a magnetic coupling by a microbalance on the outside of the pressure chamber. The time dependant weight is recorded by a PC which also controls the magnetic coupling. The magnetic suspension balance is placed inside a heating air bath. The CO_2 is provided using compressed gas cylinders. A scheme of the setup is shown in Fig. 2.

2.4. Supercritical fluid extractions

Extractions with supercritical CO_2 were carried out in the Autoclave Engineers Screening System previously described [14]. In order to isolate essential oil fraction and investigate the influence of swelling on the dynamics of SFE, extractions from hyssop, wild thyme and mint were performed at 10 MPa and 40 °C. Plant material was milled and sieved. Fraction with the average particle diameter of 0.7 mm was used for the extractions. Flow rate of supercritical fluid was 0.3 kg/h.

Extractions from rosemary and sage leaves were performed at higher pressures in order to investigate the influence of swelling of Lamiaceae family species on the SFE yield of total extract (containing essential oil fraction as well as antioxidant fraction). Chosen extraction conditions were 40 °C and 30 MPa as well as 100 °C and 30 MPa. Fraction of milled plant material with mean particle size of 0.5 mm was used for the extractions. Supercritical fluid flow rate was 0.25 kg/h.

Extractions from valerian root were carried out at 50 °C and 15 MPa, while SFE from ginger root was performed at 40 °C and 30 MPa. While valerian root was only finely milled and sieved to mean particle diameter of 0.4 mm, ginger root was also coarsely ground (particles 0.3–3 mm in diameter) in order to investigate the influence of swelling on SFE from coarsely ground plant mate-