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SCIENTIFIC PAPER

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ENERGY SAVING IN THE SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF ESSENTIAL OILS FROM SPECIES OF THE LAMIACEAE FAMILY

The reduction of energy consumption in the supercritical carbon dioxide extraction of essential oils from leaves of species of the Lamiaceae family due to the optimal pretreatment of herbaceous material was studied in the present work. Essential oils of species of the Lamiaceae family are stored in peltate glandular trichomes on the leaf surface, and the optimal pretreatment for this type of secretory structure should include grinding followed by supercritical carbon dioxide batch (non–flow) pretreatment under extraction conditions prior to continuous flow extraction. Supercritical fluid extractions of peppermint (Mentha piperita), wild thyme (Thymus serpyllum) and hyssop (Hyssopus officinalis) leaves were performed including only grinding pretreatment as well as optimal pretreatment. The experimentally determined reductions of supercritical carbon dioxide consumption, for the observed extraction yields, ranged from 0.250 to 0.889 kg CO_2 per gram of produced essential oil extract, while the corresponding reductions of energy consumption were in the range 48–170.7 kJ per gram of produced essential oil extract.

Key words: Supercritical fluid extraction, Mathematical modelling, Essential oil, Lamiaceae family

Essential oils are complex mixtures containing volatile compounds of certain secondary plant metabolites that mostly include terpenoids and phenylpropenes. In plant material, essential oils with or without resins and gums are found in special secretory structures located within plant tissues or on the surface of the plant. The type of secretory structure is specific to the plant family or species. The process of essential oil isolation, either by extraction or distillation, should depend on the oil storage and the type of secretory structure [1]. Secretory structures on the surface of the plant are glandular trichomes, which are modified epidermal hairs that can be found covering the leaves, stems and even parts of flowers. Secretory structures within plant tissue can be secretory cells, secretory cavities or secretory ducts.

Aromatic herbs that are members of the Lamiaceae family (basil, rosemary, marjoram, oregano, peppermint, spearmint, pennyroyal, hyssop, sage, lavender, thyme etc.), possess two types of glandular trichomes on the surface of their leaves, called peltate and capitate glands [2–5]. Recent investigations [5] have shown that most (if not all) of the essential oil is found on the surface of the leaves in peltate glandular trichomes (peltate glands). On the basis of these new investigations and on the basis of the scanning electron microscopy (SEM) of a dozen different tissue samples from dried leaves of basil and peppermint, before and after treatment with supercritical carbon dioxide (SC CO_2), a new mathematical model of the SC CO_2 extraction process was developed [6,7]. According to these investigations, the fraction of peltate glands is disrupted by the grinding process, and the oil from this fraction is easily available for SC CO_2. The peltate gland membrane of the fraction that stayed untouched by the grinding is permeable for CO_2 molecules. Thus, under SC conditions CO_2 penetrates through it and dissolves in the oil phase inside the glands. This leads to a glandular volume increase and the subsequent disruption of the peltate gland membrane during the process, for the fraction of glands that stayed untouched by the grinding. This phenomenon that exposure to supercritical CO_2 led to the disruption of a fraction of peltate glands and the release of essential oil, indicated the optimal supercritical fluid extraction (SFE) process regarding the reduction of energy consumption. If the grinded plant material is exposed to SC CO_2 under the extraction conditions long enough for untouched peltate gland disruption to occur before the continuous SFE process, a quantity of SC CO_2 can be saved. Therefore, the optimal SFE process should include grinding followed by SC CO_2 batch (non–flow) pretreatment, which enables peltate gland disruption prior to continuous flow extraction [7].

In this study the reduction of energy consumption due to the optimal pretreatment of herbaceous material was investigated and experimantaly determined for SFE from leaves of three members of the Lamiaceae family: peppermint (*Mentha piperita*), hyssop (*Hyssopus officinalis*) and wild thyme (*Thymus serpyllum*).

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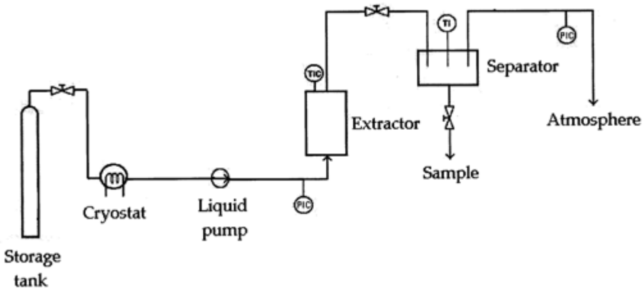

Figure 1. Schematic presentation of The Autoclave Engineers Screening System

EXPERIMENTAL

Materials and equipment

Dry leaves of peppermint (*Mentha piperita*), hyssop (*Hyssopus officinalis*) and wild thyme (*Thymus serpyllum*) grown in northern Serbia were used in the experimental studies. Peppermint leaves were dried at room temperature for 15 days, packed and kept in a dark and cold place prior to the experimental studies. Experiments with peppermint were performed in the spring, and leaves from the 2004 harvest were extracted. Experiments with hyssop and wild thyme were carried out in summer and leaves from the 2005 harvest were used.

Extractions with SC CO_2 were carried out in an Autoclave Engineers Screening System shown in Figure 1. The Supercritical Extraction Screening System is designed for small batch research runs using CO_2 as the supercritical medium with a maximum allowable working pressure of 41.3 MPa at 511 K. Liquid CO_2 is supplied from a CO_2 cylinder by a siphon tube and cooled in a cryostat between the cylinder outlet and the pump to prevent vaporization. The CO_2 is then pumped into the system until the required pressure is obtained. Back pressure regulators are used to set the system pressure (in the extractor and separator). The extractor vessel is filled with the plant material from which the essential oil is to be extracted. Heaters are supplied on the extractor vessel for temperature elevation. The SC CO_2 flows through the extractor and enters the separator vessel. Samples of the extracted substance can be taken by opening the ball valve located at the bottom of the vessel. The CO_2 continues to flow out of the separator through the flowmeter/totalizer and out to the atmosphere.

Methods

Dry leaves of peppermint, hyssop and wild thyme were ground and sieved. The fraction with an average particle size of 0.7 mm was used for the experimental studies. SFEs were carried out at 313 K and 10 MPa. In the first experiment the continuous extraction process started immediately after the system reached the extraction conditions (313 K, 10 MPa). In the second experiment the ground herbaceous material was first exposed to SC CO_2 at the extraction conditions for an hour, as a pretreatment, prior to continuous flow extraction. The SC CO_2 flow rate was 0.30 kg/h and the sample mass was 30 g for peppermint and 14 g for hyssop and wild thyme. The amount of total extract was measured during the extraction. The reduction of SC CO_2 consumption was experimentally determined. On the basis of these experimental data the reduction of the energy consumption for a fixed extraction yield was calculated. The reduction of energy consumption included energy savings in the following process sections: the cooling of CO_2 from the storage tank (room temperature – 293 K and 5.7 MPa) in front of the entrance to the high pressure liquid pump (268 K and 5.7MPa), and the compression and heating of liquid CO_2 (268 K and 5.7 MPa) to the supercritical fluid state (313 K and 10 MPa). The enthalpies of liquid and supercritical CO_2, used for these calculations, are presented in Table 1.

Table 1. CO_2 enthalpies (adopted from Temperatur – Entropie Diagramm für Kohlensäure (CO_2), CARBO–Kohlensäurwerke GmbH & Co.KG)

T (K)	293	268	313
P (MPa)	5.7	5.7	10
h (kJ/kg)	748	680	807

RESULTS AND DISCUSSION

The results of the experiments performed with the aim to investigate the advantage of SC CO_2 pretreatment in the case of SFE from the ground leaves of peppermint, hyssop and wild thyme are presented in

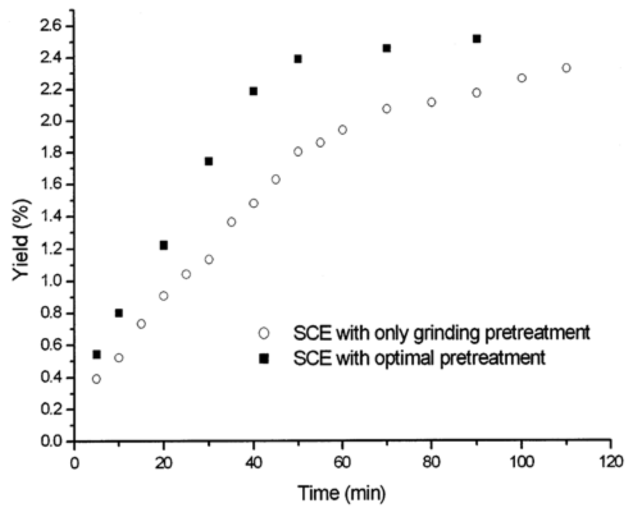

Figure 2. Comparison of the SFE processes from peppermint leaves at 313 K and 10 MPa

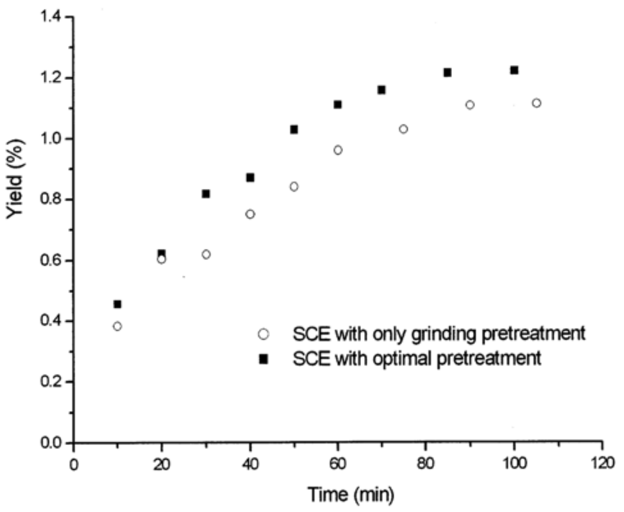

Figure 3. Comparison of the SFE processes from hyssop leaves at 313 K and 10 MPa

Table 2. Experimentally determined SC CO_2 savings and corresponding reductions of energy consumption

Herb (SCE conditions)	SC CO_2 reduction (kg CO_2/g SFE extract)	Reduction of energy consumption (kJ/g SFE extract)	Extraction yield (%)
Peppermint (313 K, 10 MPa)	0.250	48.0	2.00
	0.317	60.8	2.10
Hyssop (313 K, 10 MPa)	0.611	117.1	0.90
	0.822	157.8	1.00
Wild thyme (313 K, 10 MPa)	0.660	126.7	0.80
	0.889	170.7	0.90

Figs. 2, 3 and 4, respectively. As can be seen, much more total extract was collected during the first forty minutes of extraction when the SC CO_2 pretreatment procedure was applied. During the SFE process from ground plant material without SC CO_2 pretreatment, an increase in the slope of the extraction yield curve can be observed around 30 minutes of extraction (Figs. 2, 3 and 4). This increase is due to the newly released oil from the glands disrupted because of CO_2 dissolution and gland membrane stretching during the process. The SFE from the plant material that underwent SC CO_2 pretreatment, as well as grinding pretreatment, is characterized by higher values of the extraction yield during the process (Figs. 2, 3 and 4). Also, there is no sudden increase of the slope of the extraction yield curve as in the case of the SFE from the plant material that underwent only grinding pretreatment. These results confirmed that peltate gland disruption occurred during the SC CO_2 pretreatment. The experimentally determined reductions of the SC CO_2 consumption per

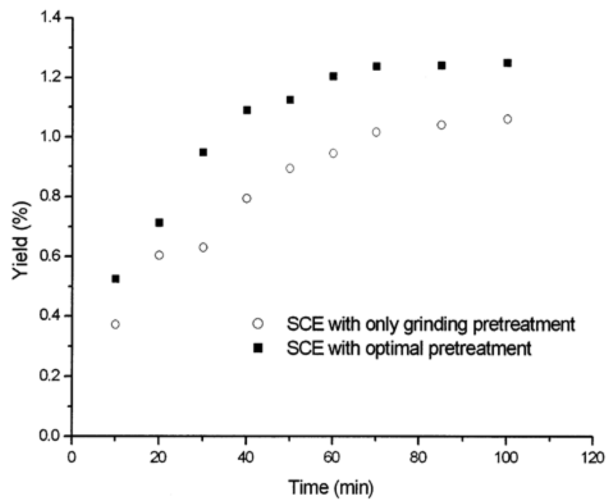

Figure 4. Comparison of the SFE processes from wild thyme leaves at 313 K and 10 MPa

unit mass of produced essesntial oil extract for two values of the extraction yield are presented in Table 2, for each herb. The calculated values of the corresponding reductions of energy consumption are also presented. The determined reductions of SC CO_2 were ranged from 0.250 to 0.889 kg CO_2 per gram of produced essential oil extract, while the corresponding energy savings were in the range 48–170.7 kJ per gram of produced essential oil extract.

CONCLUSION

The advantage of optimal pretreatment in the SFE of essential oils from species of the Lamiaceae family was experimentally proved and quantified in the case of the SFE of pepermint, hyssop and wild thyme leaves. The same phenomenon is to be expected for the essential oil SFE of each member of the Lamiaceae family characterized by peltate glands as essential oil reservoirs. Since processes under high pressures are characterized by high operating costs, the estimated values of the SC CO_2 savings, and the corresponding energy savings are significant on an industrial scale.

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IZVOD

UŠTEDA ENERGIJE U PROCESIMA EKSTRAKCIJE ETARSKIH ULJA BILJAKA FAMILIJE LAMIACEAE NATKRITIČNIM UGLJEN DIOKSIDOM

(Naučni rad)

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U radu je ispitana mogućnost uštede energije u procesima ekstrakcije etarskih ulja biljaka familije Lamiaceae natkritičnim ugljen dioksidom, usled optimalnog predtretmana biljnog materijala. Kod biljaka ove familije, etarska ulja se nalaze u peltate glandularnim trihomima na samoj površini lista. Optimalan predtretman za ovaj tip sekrecione strukture uključuje, pored procesa mlevenja, i izlaganje mlevenog biljnog materijala kao šarže natkritičnom ugljen dioksidu na radnim uslovima, pre početka kontinualne ekstrakcije. Natkritične ekstrakcije etarskih ulja lista mente (*Mentha piperita*), majčine dušice (*Thymus serpyllum*) i izopa (*Hyssopus officinalis*) izvedene su sa optimalnim predtretmanom biljnog materijala, kao i sa predtretmanom koji je uključio samo mlevenje. Eksperimentalno određene vrednosti uštede natkritičnog rastvarača, za postizanje određenog prinosa, se nalaze u opsegu 0.250–0.889 kg CO_2 po gramu proizvedenog ekstrakta, dok se odgovarajuće vrednosti uštede energije nalaze u opsegu 48–170.7 kJ po gramu proizvedenog ekstrakta. Pošto procese pod visokim pritiscima karakterišu visoki operativni troškovi, ostvarene uštede energije optimalnim predtretmanom biljnog materijala su bitne na industrijskom nivou.

Ključne reči: Natkritična ekstrakcija, Matematičko modelovanje, Etarsko ulje, Lamiaceae