Supercritical Carbon Dioxide Extraction Of Hop Pellets

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The results of supercritical fluid extraction (SFE) of hop pellets performed using carbon dioxide as solvent (SC CO_2) at 290 bars and 313-333 K are presented in this study. Obtained yield of extract was approximately 20% (mass of extract/mass of plant material). Different mathematical models were checked to verify experimental results. Diffusion coefficients of the order 10^{-11} – 10^{-13} m^2/s were calculated as main parameter of used mathematical models. This calculation was result of the best fitting of data presented as yield versus consumed mass of SC CO_2.

Swelling of hop pellets under the influence of SC CO_2 is also discussed, as well as sorption/desorption experiments realized in a high-pressure view chamber which contains the precise gravimetric measuring device. Applying Crank's law of diffusion, the values of diffusion coefficients were determined for the sorption, as well as for the desorption process. These results showed considerable influence of SC CO_2 on hop pellets swelling changing its transport properties.

1. Introduction

Supercritical carbon dioxide (SC CO_2) has been used over the years as the most desirable solvent for obtaining extract from hop, which is primarily consumed in the brewing industry [1-3]. It is cheap, non-toxic, non-flammable, and easy removed from the product. The process itself is realized at mild temperatures which enable chemical stability of active components of the extract. These investigations were conducted in order to obtain hop extract which could be used in industrial facilities instead of the hop itself. The usage of hop extract has certain advantages: it is stable at room temperatures, the storage of hop extract is less energy consuming, and it is easier for manipulation [3]. It was found that components present in extract, which are essential for brewing industry, could be obtained at pressure higher than 200 bar, and from 313 to 423 K [1,2].

Besides process parameters, such as pressure, temperature, flow rate etc, swelling of plant material is an aspect that has been also payed attention in recent investigations of the supercritical fluid extraction preocess [4]. 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 SFE process.

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In this work the influence of temperature on the extraction yield was studied for process of SFE from the hop pellets. Different mathematical models were checked to verify experimental results. Swelling of hop pellets under the influence of SC CO_2 is also discussed, based on swelling and sorption/desorption experiments realized in a high-pressure view chamber which contains the precise gravimetric measuring device. Applying Crank's law of diffusion, the values of diffusion coefficients through the hop pellet were determined for the sorption, as well as for the desorption process.

2. Materials and methods

2.1 Materials

Hop pellets (type Magnum) produced from Magnum milled cones, that are exploited in the industrial facilities were supplied from the Fertilizers Research Institute, Pulawy, Poland. Commercial carbon dioxide (99% purity, Messer, Belgrade, Serbia) was used for the extractions.

2.2 Methods

2.2.1 Supercritical fluid extraction (SFE)

Extractions with SC CO_2 were carried out in an Autoclave Engineers Screening System previously described [4]

In order to investigate the influence of temperature on SFE from hop pellets, experiments were carried out at 29 MPa and 313 K, 323 K and 333 K using the mass flow rate of SC CO_2 of 0.3 kg/h. The pressure in all these experiments was unchanged since this is the pressure mainly used in industrial facilities when working with hop.

2.2.2 Mathematical modelling

Analytical solutions of two mathematical models of different origin were used to describe the obtained results from SFE experiments: 1) the widely used Sovova's model [5] and 2) model based on the analogy with heat transfer [6].

Sovova's model is derived from differential mass balance for the extractor vessel and particle of plant material. The basic concept of the model is that there are two fractions of oil inside the particle: easy accessible oil from the cells broken during the pretreatment (milling) of plan material, and oil from intact cells protected by cell wall. Thus, there are two periods of SFE: the first period is so called "fast period" at the beginning of the process when easy accessible oil is being extracted, and the second period is "slow period" when extraction from intact cells is taking place. Analytical solution of model equations is possible when the second period is characterized by very large resistance to mass transfer.

The model based on the analogy with heat transfer considers a particle of a plant material as a hot ball cooling in a uniform medium (the hot ball model). Assuming that the components to be extracted are uniformly distributed inside the particle, and by applying Fick's second law of diffusion, the heat transfer analogy and the Fourier transforms, a simple equation is obtained representing the mass of extracted substance as a function of time. The model is attractive since it has only one adjustable parameter, the diffusion coefficient. On the other side, the main disadvantage of this model is that it assumes that all particles of the plant material are at the same stage of extraction process throughout the extractor vessel.

2.2.3 Swelling detection

Swelling of plant tissues was analyzed and detected optically inside a high-pressure view chamber (Pmax = 35 MPa, Tmax = 473 K) purchased from Eurotechnica and presented in Figure 1. A solid sample of hop pellet 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 and connected to a PC. A relative size change (d/d_0) of the plant material was determined. The swelling of hop pellet was observed at 29 MPa and 323 K.

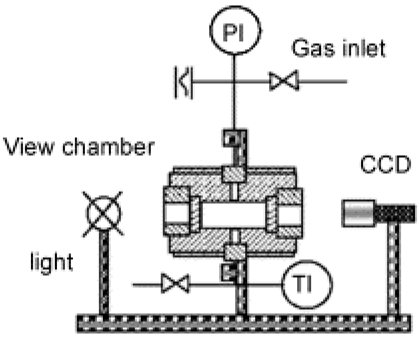


Figure 1. Schematic presentation of high-pressure view chamber.

2.2.4 Sorption/desorption of CO_2

A high-pressure gravimetric measuring device (Rubotherm, Germany) connected to a high-pressure view chamber (Pmax = 35 MPa, Tmax = 393 K, Eurotechnica, Germany) for quantifying weight under elevated CO_2 pressure and simultaneously observing phase behaviour 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 and 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. The 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. A scheme of the setup is shown in Figure 2.

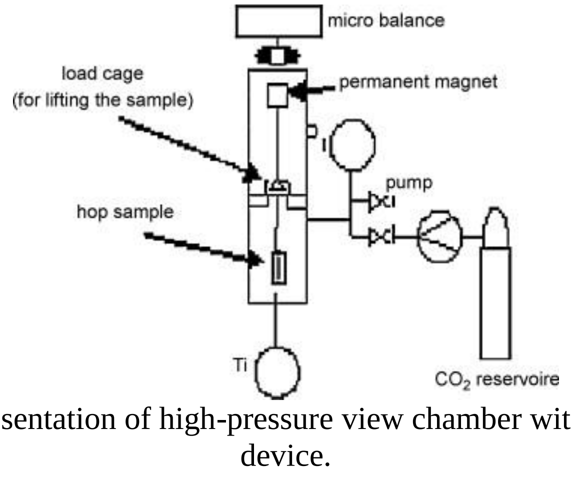


Figure 2. Schematic presentation of high-pressure view chamber with gravimetric measuring device.

3. Results

3.1 SFE and mathematical modelling

Influence of temperature on SFE from hop pellets at 29 MPa can be seen on Figure 3. The highest yield (app. 21 %) was obtained at 323 K, while the yields at 313 K and 333 K were slightly lower (17 % and 18.5 %, respectively). It is known that the density of the supercritical fluid, and consequently the solubility of solute in it, is decreasing, while the vapor pressure of the solute is increasing with increase of temperature. Such effects could be used to explain why the highest yield was obtained at 323 K. When comparing yields at 313 and 323 K, the conclusion is that the increase of vapor pressure prevails over decrease of density and, thus, the solubility and yield are higher at higher temperature. On the other hand, when comparing results at 323 and 333 K, the effect is obviously reverse.

The dynamic of the SFE from hop pellets can also be discussed on the basis of experimental results. It is obvious that the first period of the extraction is represented as fast step of extraction process. This period indicates that there is some amount of oil easy accessible to SC CO_2. A fair conclusion is that this part of the oil has been liberated from its secretory structure during the pretreatment (milling) of plant material or simply during pressurization of the extractor vessel when SC CO_2 penetrates inside the secretory structure and dissolves in the oil, thus practically pushing it out from the secretory structure.

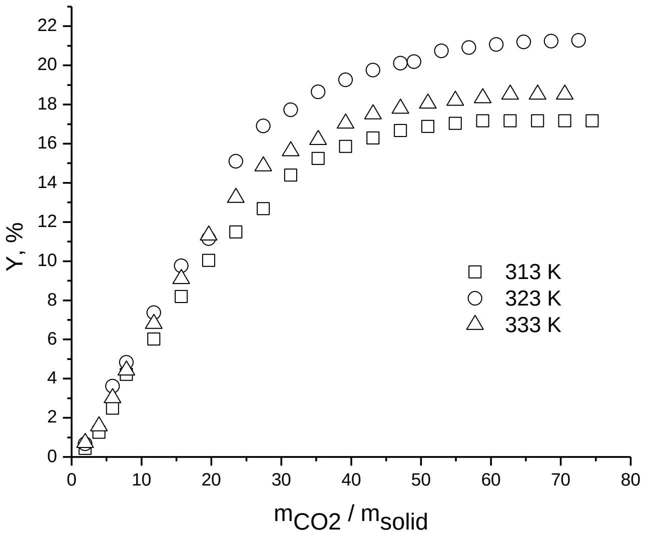


Figure 3. Results of SFE experiments with hop pellets at 29 MPa and different temperatures.

Figure 4. shows the results of applying the two mathematical models, described earlier, on results of SFE experiments. Parameters of both models are given in Table 1. Optimization was carried out according to the formula:

$$J = \left(1/m\right)\sum_{j=1}^{m}\left(Y_j - Y_{\mathrm{mod},j}\right)^2 \qquad (1)$$

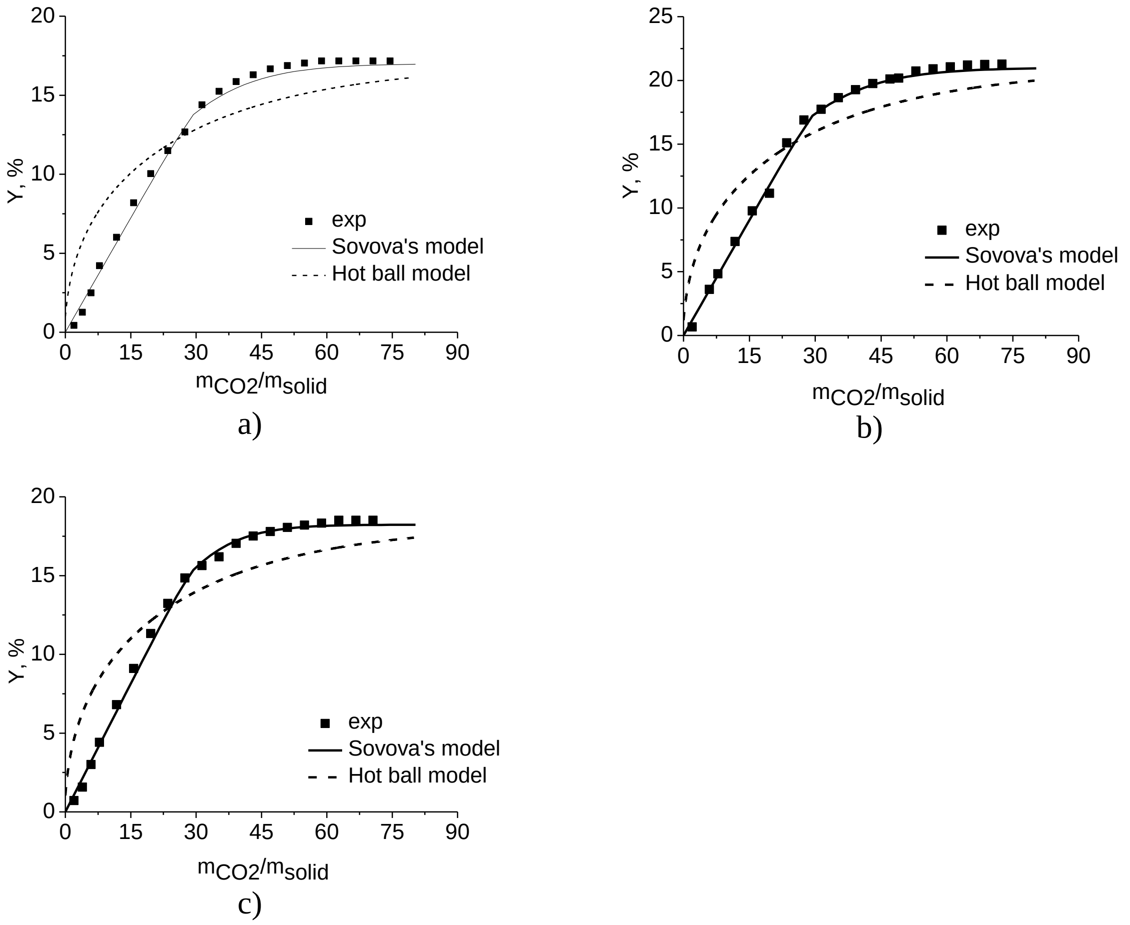
where m is the number of experimental points, Y_j is the yield determined by experimental point *j*, and $Y_{mod,j}$ is the yield obtained by the model in point *j*.

Table 1. Main parameters of mathematical models used in this study.

	P, MPa	**T, K**	**$y_r \cdot 10^3$, kg/kg**	**$k_s \cdot 10^8$, m/s**	**$D \cdot 10^{13}$, m^2/s**	***J***
Sovova's model	29	313	4.0	5.7	-	0.175
		323	5.0	6.7	-	0.146
		333	4.5	8.7	-	0.128
Hot ball model		313	-	-	4.1	5.620
		323	-	-	4.2	7.304
		333	-	-	4.3	6.244

where y_r is the solubilty of extract in the supercritical fluid k_s is the mass transfer coefficient through the solid particle of plant material and D coefficient for diffusion through the solid particle of plant material.

It is evident that Sovova's model is in a much better agreement with experimental results and that it simulates, with a higher accuracy, both, the fast and the slow period of the extraction process. The hot ball model, on the other hand, gives not so good results. The reason for this is probably in the number of fitting parameters, as well as in its main assumptions, that all particles in the same time are at the same stage of extraction and that the intraparticle diffusion is the limiting factor for the whole SFE process. The later assumption is obviously not suitable since experimental results are implying a constant slope of the modelling curve in the first part of the extraction, indicating that the increase of yield in this period is limited by solubility in SC CO_2 and not by intraparticle diffusion.



a)

b)

c)

Figure 4. Modelling results for SFE from hop pellets at: a) 313 K; b) 323 K; c) 333 K

3.2 Swelling detection

Swelling behaviour of hop pellet can be seen in Figure 5. It's evident that there is considerable swelling of hop pellet during the exposure to supercritical fluid. As can be seen, the swelling of pellets occurred immediately after pressurization. The relative change in thickness of hop granulate was around 27% as shown in Figure 6. These are important results for practical usage of SFE process since there is evidence of hardening of hop extraction cake in industrial facilities.

Figure 5. Images of hop pellet before (upper image) and during (lower image) the exposure to supercritical carbon dioxide

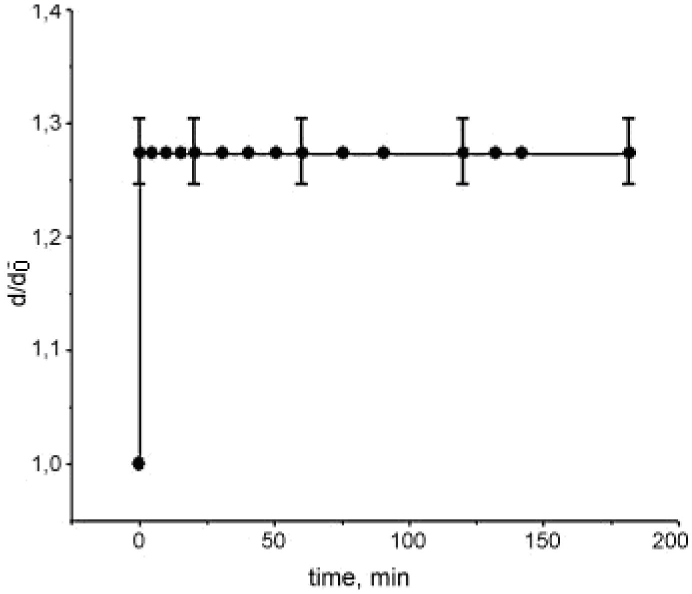
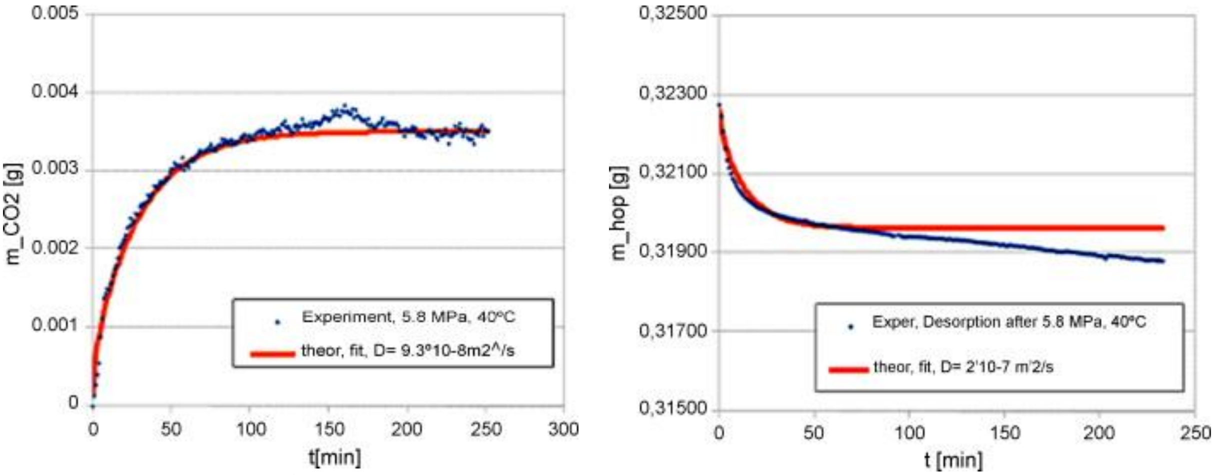


Figure 6. Relative change in thickness of the hop pellet during exposure to SC CO_2.

3.3 Sorption/desorption of CO_2

Figure 7a show the increase in weight of sample of pelletized hop related to its starting weight which is attributed to sorption of carbon dioxide since extraction can be neglected at this rather low pressure. A theoretical fit according to Fick´s law of diffusion was used to calculate the diffusion coefficient of CO_2 within the hop pellet from the experimental data on sorption kinetics. The solubility of CO_2 within the solid matrix of about 1.1 mas% of the hop pellet was calculated using data presented in Figure 7a. From a theoretical fit, the diffusion coefficient was calculated being $9.3 \cdot 10^{-8}$ m^2/s.



a) b)

Figure 7. Sorption and desorption of CO_2 from and into the hop pellet: a) sorption at 5.8 MPa and 40 °C, b) desorption after decompression from 5.8 MPa, 40 °C.

The amount of CO_2 released from the hop pellet matrix after the rapid decompression is shown in Figure 7b as a function of time. The diffusion coefficient in hop pellet was one order of magnitude higher compared to the value determined according to the sorption analysis. The reasonable conclusion from this data is that the swelling of hop pellet increases the rate of diffusion through the hop pellet expressed by one order of magnitude higher value of diffusion coefficient.

4. Conclusion

Experiments in which the effect of temperature on extraction yield for SFE from hop pellets was studied showed that 323 K is the best condition for this process at 29 MPa. The mathematical model defined by Sovova showed very good agreement with experimental results, confirming the existence of two periods of extraction process: the first is the fast period at the beginning of the extraction process when easy accessible oil is mainly extracted, and the second is slow period when oil extraction is governed by the rate of intraparticle diffusion which start to be the main resistance which define the overall rate of extraction process. The hot ball model did not fit well the experimental data as the Sovova’s model, proving that its main assumptions are not valid for the case of SFE from the hop pellets. The swelling experiments showed that there is a considerable influence of SC CO_2 on swelling of hop pellets and that the diffusion coefficient which define the mass transfer rate through the pellet is greater for one order of magnitude for the exposed than for non exposed plant material.

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